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EVALUATION OF ANTIOXIDANT ACTIVITY BY STABILIZATION OF VITAMIN A AND CAROTENE[1]

By H. J. Lips[2] and W. D. McFarlane[3]

Abstract

Accelerated tests for antioxidant activity are described which depend on the protection of vitamin A concentrates (in ethylene dichloride solution) against ultraviolet irradiation, and on the protection of carotene (in mineral oil solution) against heat and aeration. The protection of vitamin A was influenced by light-filtering effects; the carotene method appeared to be more generally useful. The stabilizing power of wheat-germ oil for both solutions of Vitamin A and carotene against light is partly due to a screening effect by pigments. Some of the protection is also due to other components of the wheat-germ oil, but it is not known whether these function as stabilizers against light according to the usual theories of antioxidant action. Light-accelerated decomposition of vitamin A and carotene appeared more suitable for special tests than for general evaluation of antioxidants; stability experiments in the absence of light gave a more generally applicable picture of antioxidant activity.

Introduction

The most important form of spoilage in edible fats and oils is oxidative rancidity, produced by the action of atmospheric oxygen. The first stage in the process of spoilage, addition of oxygen to unsaturated carbon-to-carbon linkages to form peroxides, can be delayed for long periods by addition to the fat of minute amounts of foreign materials called antioxidants. The efficacy of these antioxidants is generally determined by accelerated stability tests of the fat under carefully controlled conditions, to reduce the time necessary for development of rancidity to a convenient interval. However, ease of oxidation of fats depends on their structure and on the nature of their contained fatty acids (8, p. 86), so a method of estimating relative activities of antioxidants independently of fats should prove of value in obtaining a more absolute comparison of antioxidant potencies.

Since carotene and vitamin A are unsaturated carbon compounds of constant identity found intimately associated with fats and oils, since their destruction tends to parallel the formation of peroxides and the breakdown of naturally occurring stabilizers in the fats (6; 8, p. 80; 11; 16; 17), and

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[2] *Biochemist, Oils and Fats Laboratory, Division of Applied Biology, National Research Laboratories, Ottawa, Canada.*

[3] *Director of Research, Canadian Breweries Ltd., Toronto, Canada.*

since they can be preserved by the addition of antioxidants (e.g., 2, 3), the use of these compounds for measurement of antioxidant activity readily suggests itself.

The stability of carotene and vitamin A has often been studied in fats and fatty materials containing antioxidants (e.g., 12, 18). However, fewer experiments have been reported on the testing of antioxidants for these substances in pure solvents. Williams (19) stored solutions of carotene plus stabilizers in mineral oil at 75°C. Lovern (10) tested antioxidants with carotene in ethyl acetate solution, decomposition being accelerated by visible light. Parker, Neish, and McFarlane (15) estimated antioxidant potency of wheat-germ oils by the protection afforded to vitamin A concentrates in chloroform against ultra-violet irradiation. Their results suggested adaptation of this technique to general measurements of relative potencies of antioxidants.

This paper describes further experiments with the Parker–Neish–McFarlane method, and with a method involving aeration of carotene in mineral oil. The vitamin A irradiation method was examined specifically to determine if the protection afforded by pigmented antioxidants was due to interference to the passage of ultraviolet light, and the carotene method was developed because of observed shortcomings in the irradiation procedure.

Evaluation of Antioxidant Activity by Stabilization of Vitamin A

Materials and Methods

In the earlier irradiation work (15), halibut-liver oil (the vitamin A source) and wheat-germ oil (the chief antioxidant tested) in chloroform were irradiated, and vitamin A was determined at intervals in aliquots of the solutions. The irradiation apparatus consisted of a General Electric H3 mercury lamp 8 in. from a rack holding three tubes of test solutions. A No. 986 Corning filter protected the solutions from excessive heat but transmitted approximately 90% of the ultraviolet radiation at 3300 Å. The apparatus was enclosed in a well ventilated box.

In the present study this apparatus was modified to irradiate six matched tubes at one time. These (stoppered) tubes were set in evenly spaced holes around the circumference of a metal disk, which was revolved at a uniform speed to ensure that each tube was equally exposed to irradiation. The rotary apparatus was contained in a ventilated box having a window of Red Purple Corex "A" glass similar in characteristics to the filter previously used. The amount of visible light transmitted by this glass was negligible. The ultraviolet source, a Hanovia mercury quartz lamp, was placed in a larger box adjacent to the smaller one, with an opening corresponding to the size of the filter (Fig. 1). The temperature in the smaller box was within 0.3° C. of room temperature. The intensity of irradiation was varied by directing a current of air from an electric fan upon the lamp to keep down its temperature, or by changing the distance of the lamp from the filter.

In the preparation of test solutions of vitamin A plus antioxidants, ethylene dichloride was found more suitable than chloroform, since cloudiness was less likely to occur in the former solvent upon addition of antimony trichloride reagent in the vitamin A determination (13). Moreover, destruction of vitamin A in this solvent was somewhat slower than in chloroform.

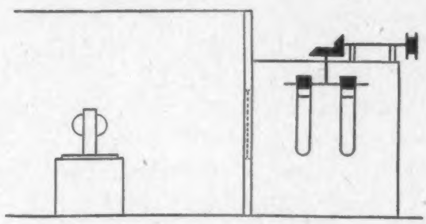


FIG. 1. *Apparatus for ultraviolet irradiation of test solutions.*

As pure vitamin A was not available, fresh, high potency halibut-liver oil was added as before to the solvents, the initial concentration of the vitamin being approximately the same in all irradiation and other stability trials—50 mgm. of oil per 100 ml. or 30 I.U. of vitamin A per ml. Aliquots of 1 ml. were removed for vitamin A determination (4). Wheat-germ oil was again the chief antioxidant used. All concentrations of antioxidants were expressed as per cent by weight of the solvent, and the amount of vitamin A remaining after irradiation as per cent of the original value. The action of antioxidants in the irradiation experiments was compared to their behavior in storage tests in daylight and in the dark.

Interference by Pigments

The possibility that the protective action of wheat-germ oil was due in part to interference by pigments to the passage of ultraviolet light (15) was investigated in several ways:

(*a*) Wheat-germ oil containing ascorbic acid was prepared by adding the acid in peroxide-free ethyl ether and removing the ether by vacuum distillation. This should increase the stabilizing power of the oil (9) without altering its light transmission.

(*b*) The possible screening effect was tested by the substitution of solutions of wheat-germ oil in a quartz cell for the Corex filter normally employed in the apparatus.

(*c*) An attempt was made to segregate the antioxidant principle of the wheat-germ oil in a *colorless* form by a method based on a procedure for vitamin E determination (14). In this method a 2% solution of the oil in petroleum ether is treated with 85% sulphuric acid. The ether layer is removed by centrifuging and decanting, and is washed with dilute potassium hydroxide solution to remove any remaining acid. (The tocopherol content

of an aliquot of the petroleum ether solution is determined by reaction with ferric iron and dipyridyl.) This procedure was carried out with a volume of wheat-germ oil several times that customarily employed in the vitamin estimation. After the alkali washing, the petroleum ether solution was dried by passage through anhydrous sodium sulphate in a sintered glass funnel, and the solvent was removed under vacuum. After several trials a pale yellow oil was obtained which corresponded in tocopherol content (2.03 mgm. per gm.) to an untreated wheat-germ oil at hand (2.05 mgm. per gm.). The treated oil imparted no detectable color to ethylene dichloride or chloroform solutions at concentrations up to 4%.

Results

Wheat-germ oil fortified with ascorbic acid was compared with untreated wheat-germ oil at various concentrations in ethylene dichloride and in chloroform, and at various intensities of irradiation. Some results are presented in Fig. 2. Ascorbic acid afforded only a slight increase in protection against ultraviolet irradiation. A comparison of the fortified and unfortified oils in regard to their protective action against *visible* light yielded similar results, i.e., after six days' storage in bright daylight, control ethylene dichloride solutions retained only 10% of the original vitamin A; ethylene dichloride solutions containing wheat-germ oil fortified with from 0 to 0.5% ascorbic

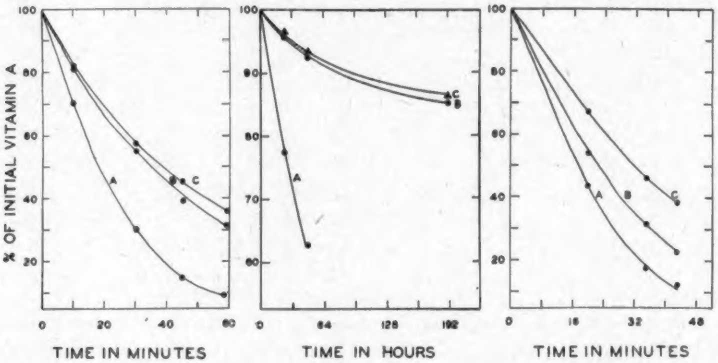


FIG. 2

FIG. 3

FIG. 4

The Protection of Vitamin A by Antioxidants

FIG. 2. *Vitamin A irradiated in ethylene dichloride; lamp distance, 12 in.; fan off.*
A *Control.*
B *Control + 1.6% wheat-germ oil.*
C *Control + 1.6% wheat-germ oil containing 0.5% ascorbic acid.*
FIG. 3. *Vitamin A in chloroform solution stored in the dark at 40° C.*
A *Control.*
B *Control + 0.4% of sulphuric acid treated wheat-germ oil.*
C *Control + 0.4% untreated wheat-germ oil.*
FIG. 4. *Vitamin A irradiated in ethylene dichloride; lamp distance, 9 in.; fan off.*
A *Control.*
B *Control + 1.6% of sulphuric acid treated wheat-germ oil.*
C *Control + 1.6% untreated wheat-germ oil.*

acid all retained about 50% of the original vitamin A. However, the fortified oils exhibited more definite superiority in stabilizing vitamin A solutions stored in the dark. For example, control solutions of vitamin A in chloroform retained 30% of original vitamin A after 17 days' storage at room temperature in the dark; solutions containing 0.05% wheat-germ oil retained 90%; and solutions containing 0.05% wheat-germ oil fortified with 0.5% ascorbic acid retained 100% of the original vitamin A.

When the filter used in the irradiation apparatus was replaced by a quartz cell containing only ethylene dichloride, the vitamin A content of ethylene dichloride solutions *in the tubes* was reduced in one hour's irradiation (fan on; lamp distance, 9 in.) to about 94% of the original value. When a 2% solution of wheat-germ oil in ethylene dichloride was placed in the quartz cell, a second set of vitamin A solutions identical with the first still retained 100% of the initial vitamin content after *two* hours' irradiation under the same conditions.

The sulphuric acid treated wheat-germ oil definitely protected vitamin A in chloroform or ethylene dichloride in the absence of light. This protection was only slightly less than that afforded by an equivalent concentration of untreated wheat-germ oil with the same tocopherol content. Examples are presented in Fig. 3. The treated oil also exerted a slight protective action for vitamin A in the irradiation test. In one test (lamp distance, 14 in.; fan off; chloroform solutions) after 70 min. irradiation, the control solutions retained 22% of original vitamin A, and solutions containing from 0.25 to 0.75% sulphuric acid treated wheat-germ oil retained from 26% to 33% of original vitamin A.

However, when comparison of the sulphuric acid treated wheat-germ oil with the untreated wheat-germ oil of corresponding tocopherol content was made under varying conditions of irradiation, the greater protective action of the untreated oil was more pronounced than in the absence of light (Fig. 4). A similar result was noted when the two oils were compared for protective action against visible light. Control ethylene dichloride solutions in indirect daylight retained 60% of original vitamin A after 12 days; solutions containing 1.6% untreated wheat-germ oil retained 100%; and solutions containing 1.6% treated wheat-germ oil retained 90% of original vitamin A.

Discussion

The absence of a definite induction period in the light-induced decomposition of vitamin A in the presence of antioxidants is noteworthy (Figs. 2-4). It is possible that oxidation of vitamin A in the halibut liver oil used in these experiments had already begun, even though the oil itself was freshly purchased. The addition of an antioxidant after oxidation had begun would have little tendency to produce a definite induction period, although some degree of protection might be obtained (15). Zilva (1) observed that ascorbic acid in aqueous solution was rapidly changed to the dehydro form under the influence of ultraviolet light. This may help to explain the failure of ascorbic

acid to increase appreciably the stabilizing action of wheat-germ oil for vitamin A in the irradiation experiments. The vitamin A experiments were complicated by the presence of halibut liver oil; the use of pure vitamin A in such tests would be desirable. However, all the results indicated that light-accelerated tests had limited application, since interference to the passage of light by the antioxidants tested was an important factor in protecting vitamin A in solution.

Evaluation of Antioxidant Activity by Stabilization of Carotene

Materials and Methods

Stabilization experiments with carotene and antioxidants were first tried in the ultraviolet irradiation apparatus described in the previous section. S.M.A. carotene*, containing approximately 5% alpha-carotene and 95% beta-carotene, was used. The carotene was irradiated in petroleum ether solution in stoppered colorimeter tubes which were removed at intervals for readings with the Evelyn colorimeter at 440 mμ, to determine the amount of destruction of carotene.

Storage of carotene in petroleum ether solution at room temperature in the absence of light was also attempted. In addition, carotene solutions in mineral oil, with the addition of various fat-soluble antioxidants, were aerated and heated in the dark under the conditions of a modified Swift stability test (9). In place of the all-glass aspirators usually employed, colorimeter tubes were used for the carotene solutions, and lengths of glass tubing were used for aeration. Color readings were made directly on the mineral oil solutions at intervals, the carotene tubes being read while hot and then returned to the apparatus at once. Initial concentrations of approximately three gamma of carotene per ml. of mineral oil were used and the amount remaining after aeration was expressed as per cent of the original value. The concentrations of antioxidants, given as per cent by weight of the mineral oil, were selected so that pigmented stabilizers did not add any measurable color to the carotene solutions. The antioxidants were added in peroxide-free ethyl ether as in the modified Swift stability test (9).

Results

Preliminary experiments showed that carotene was not stabilized against the action of ultraviolet light by antioxidants of the wheat-germ oil type when the stabilizer did not add to the color of the original carotene solution. In some trials the added antioxidant appeared to accelerate bleaching of the carotene.

Decomposition of carotene in petroleum ether in the dark at room temperature was very slow. However, it was found that addition of catalytic quantities of benzoyl peroxide would speed up decomposition markedly. The most satisfactory method was evolved when carotene in mineral oil solution was heated and aerated in the absence of light under the conditions of the

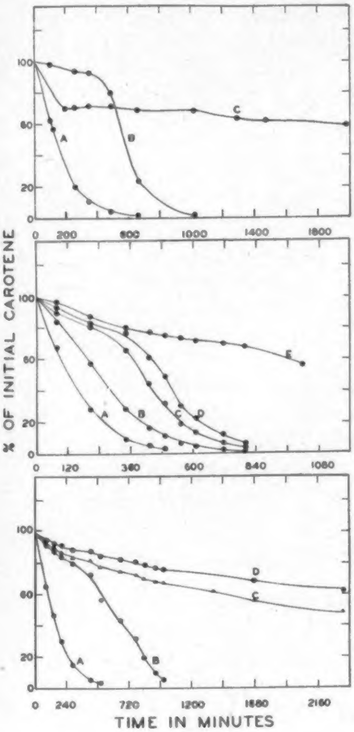
*S.M.A. Corporation, Chagrin Falls, Ohio.

Swift stability test. Retention of original carotene checked closely in duplicate trials (within 1% of the original content), and added antioxidants appeared to behave in a normal fashion.

Fig. 5 presents a comparison of the action of wheat-germ oil and a sulphuric acid treated wheat-germ oil, both of the same tocopherol content (2.03 mgm. per gm., see above), in stabilizing carotene in the aeration test. The curve for wheat-germ oil showed a well defined induction period, with destruction proceeding at the same rate as in the control sample when the stage of rapid bleaching had been reached. With the sulphuric acid treated oil there was a sharp initial decrease in carotene concentration, with a slow subsequent deterioration.

To determine if the characteristic induction period would be obtained when carotene was protected by a pure substance, the effect of different concentrations of citric acid was examined. Fig. 6 shows that protection by citric acid did give rise to a definite induction period.

Fig. 7 illustrates the protection of carotene by gum guaiac, a complex phenolic substance. Here again the carotene was strongly stabilized.



FIGS. 5-7

The Protection of Carotene by Antioxidants

FIG. 5.
A Control.
B Control + 0.1% untreated wheat-germ oil.
C Control + 0.1% of sulphuric acid treated wheat-germ oil.

FIG. 6.
A Control.
B Control + 0.001% citric acid.
C Control + 0.002% citric acid.
D Control + 0.003% citric acid.
E Control + 0.10% citric acid.

FIG. 7.
A Control.
B Control + 0.002% gum guaiac.
C Control + 0.01% gum guaiac.
D Control + 0.02% gum guaiac.

Discussion

The initial rapid destruction of carotene in the presence of sulphuric acid treated wheat-germ oil (Fig. 5) may have been due to the initial presence of some oxidizing impurity which was reduced by the antioxidant. The final high degree of protection given by the concentrate was surprising, since it probably did not contain stabilizing constituents other than tocopherols. Since the antioxidants of wheat-germ oil could function either by protecting carotene directly from the oxygen of the air, or by inhibiting formation in the wheat-germ oil of peroxides which would destroy carotene, the greater protective action of the sulphuric acid concentrate over that of the wheat-germ oil may have been due to elimination of the more unstable components of the wheat-germ oil.

The stability curves obtained when stabilizers were added to carotene in the aeration test showed an induction period, suggesting that the antioxidant was functioning in a normal fashion. The existence of colored oxidation products of carotene has been noted (1, 7), and formation of such substances could affect the usefulness of this method. However, the regularity of the decomposition curves suggests that if such products were formed they were subsequently broken down in a regular fashion to colorless compounds. The carotene aeration method would therefore appear to offer a simple means of comparing antioxidant activities.

Conclusions

It is concluded that the vitamin A and carotene stabilizing power of wheat-germ oil in the presence of light is partly due to a screening effect by pigments. Part of the activity also resides in the nonchromogenic material, but it is not known whether this functions as a stabilizer against light according to the usual theories of antioxidant action. Since constituents of wheat-germ oil such as sterols, tocopherols, and unsaturated fatty acids absorb ultraviolet light, some of this protection may also be of a physical nature.

In view of the complex nature of the protection afforded against the action of light by wheat-germ oil, and of the anomalous results obtained in vitamin A protection with ascorbic acid fortified oil and with sulphuric acid treated oil, the irradiation method and other methods depending on exposure to light appeared to be more suitable for special tests than for general evaluation of antioxidants. Stability experiments in the absence of light yielded a more generally applicable picture of antioxidant activity.

Comparison of antioxidants by their protection of carotene in heated, aerated mineral oil in the absence of light appeared to be convenient, since pure carotene can be obtained, and the destruction of carotene can be easily measured. A comprehensive study of a series of antioxidants by the carotene method would be necessary to determine if results obtained for the conjugated double bond system of carotene could be directly applied to the stabilization

of the ethenoid unsaturates of complex natural fats. The preliminary experiments indicate that, with pure antioxidants at least, valuable information might be secured regarding their protective properties by use of the carotene aeration procedure.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XIV. THE CAUSE OF THE EEFECT OF HYDROGEN SULPHIDE TO REDUCE THE COMPRESSION RATIOS AT WHICH FUEL GASES CAN BE USED IN SPARK IGNITION ENGINES[1]

BY R. O. KING,[2] E. J. DURAND,[3] BERNARD D. WOOD,[4] AND A. B. ALLAN[5]

Abstract

Experimental results are given for trials of the C.F.R. engine at 900 r.p.m. and 12 : 1 C.R. on Toronto town gas alone and with an addition of hydrogen sulphide. The sulphide led to such severe preignition that measurements of power were impossible except for very weak or very rich mixtures. The former included the 50% weak mixture for which thermal efficiency is a maximum. The sulphide was then of beneficial effect, a maximum value of 44% for indicated thermal efficiency being obtained as compared to a maximum of 42.5% without it. The experimental results are interpreted in the light of combustion tube experiments showing that hydrogen in mixtures with air is not ignited by red hot surfaces on which it is oxidized with sufficient rapidity to steam, but that ignition occurs at relatively low temperatures if the surface reaction is inhibited by hydrogen sulphide. The conclusion is that fuel gases containing hydrogen in large proportion can be used for full power engine operation at compression ratios even higher than 12 : 1 if the oxidation of the hydrogen in part to steam, on the hot surfaces in the combustion chamber, is not inhibited by the poisoning effect of the hydrogen sulphide commonly present in the gases.

Introduction

The compression ratio of 12 : 1 at which Toronto town gas was used for the engine trials described in Part XIII (7) is impossibly high according to accepted standards. Ricardo, for example, states (15, p. 32) that the usable compression ratio for town gas is 5 to 6 : 1, for producer gas 6 to 7 : 1, for blast furnace gas 7 to 7½ : 1, and for coke oven gas which frequently contains over 50% of hydrogen the safe compression ratio is little if any greater than 5 : 1. Lucke is even more specific in respect of the role played by hydrogen. He states (12, p. 33), "gases rich in hydrogen generally preignite easily; approximately one atmosphere should be deducted from the compression allowable with no hydrogen for each 5 per cent of hydrogen present". The "safe" compression pressure given accordingly in Kent (4, 12-41) is 90 to 100 lb. per sq. in. gauge for coke oven gas which contains hydrogen in greater concentration than is found in other fuel gases. The views mentioned in respect of hydrogen appear to be confirmed by the experiments of Ricardo (16) and A. F. Burstall (2). Their experiments are discussed at some length

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Contribution from Defence Research Board in association with the Department of Mechanical Engineering, University of Toronto, Toronto, Ont.
[2] *Research Scientist, Defence Research Board, Ottawa, Canada.*
[3] *Lecturer, Department of Mechanical Engineering, University of Toronto.*
[4] *Assistant Professor, Department of Mechanical Engineering, University of Manitoba, Winnipeg, Manitoba.*
[5] *Research Assistant, Department of Mechanical Engineering, University of Toronto.*

by Pye (14, pp. 188-190) who after describing the operation of the E 35 engine on extremely weak hydrogen–air mixtures concludes, "the same faculty of rapid flame propagation which makes burning possible on the weak side, makes it impossible to work at the rich end of the scale of fuel–air ratios even up as far as the correct mixture. Whenever running was attempted with a hydrogen–air ratio more than about 95 per cent of that giving complete combustion, violent preignition set in, accompanied by firing back through the carburetor. This happened even when the compression ratio was lowered to 3.8 : 1 while at higher ratios smooth running was limited to even weaker mixtures."

The experimental results for engine trials with hydrogen and town gas, described in Parts V (10), VI (11), XII (6) and XIII (7), are completely at variance with those presently accepted as a basis for the authoritative conclusions mentioned above. Hydrogen has been used at compression ratios extending to 10 : 1 at any mixture strength and without preignition (10); town gas containing hydrogen in a concentration nearly as great as in coke oven gas has been used similarly at a compression ratio of 12 : 1 (7), the compression pressure then being 390 lb. per sq. in. gauge as compared with the "safe" value of 80 to 100 lb. given in "Kent". Moreover, the performance in respect of power and thermal efficiency was commensurate with the unusually high values of the compression ratio which at 12 : 1 was just within the Diesel engine range. It is indicated accordingly, and is illustrated by the experiments of Part XIII (7), that the spark ignition Otto cycle engine may be made to surpass the Diesel in respect of both power and thermal efficiency. It is thermodynamically possible because both types now use the Otto cycle, and combustion characteristics are the better for the carburetor spark ignition type.

The great increase in power and thermal efficiency obtainable by using fuel gases at Diesel engine compression ratios would be of economic importance if it could be realized in practice. It may be considered, therefore, that the object of the investigation presently in hand is in part to discover why it has been necessary to operate the spark ignition gas engine at the relatively low compression ratios for which power and thermal efficiency are necessarily inferior. The experimental results described in earlier Parts provide a partial explanation only. The experiments of this Part were planned in the hope of completing the explanation.

It was shown by the experiments with hydrogen alone, Part V (10), that preignition accompanied by firing back through the carburetor was due to ignition of the hydrogen–air mixture by finely divided carbon derived from the decomposition and oxidation of the lubricating oil, but starting with a clean engine some hours running was required for the necessary accumulation of carbon. On the other hand, the decomposition and oxidation of the lubricating oil did not yield finely divided carbon to the same extent when Toronto town gas was used as engine fuel, as oted in Part XIII (7). It

seemed that the engine would run for an indefinite period without preignition if a normal jacket temperature were maintained. Such a result, according to experience in practice, would be an impossibility if coke oven gas were used although the proportion of hydrogen in it is not substantially greater than in Toronto town gas. The gases differ mainly in respect of sulphur concentration. Toronto town gas is nearly free of hydrogen sulphide and contains organic sulphur in the extremely small concentration of 10 to 15 grains per 100 cu. ft., as mentioned in Part XIII (7), whereas the concentration in coke oven gas may be as great as several hundred grains per 100 cu. ft. and may extend to several thousand in refinery gases from sulphur crudes and in natural gases from sulphur bearing regions (13, p. 2362).

It appears, therefore, that hydrogen sulphide is the chief sulphur impurity in fuel gases. It is known that the substance promotes preignition, and the experiments of this Part were made to determine the extent and cause of the effect.

Experimental Arrangements and Results

The experimental arrangements were as described in Part XIII (7) plus means for adding hydrogen sulphide at a measured rate to the air–gas mixture. The hydrogen sulphide was obtained from the Matheson Co. in a high pressure steel cylinder from which it was drawn as required through a special pressure regulator. It was supplied at atmospheric pressure at the rate of 4.8 cu. ft. per hr. to the air–gas mixture used by the engine. The rate was the minimum that could be measured accurately by the available dry gas meter and is approximately 5.0% by volume of the rate of town gas required for maximum power.

The hydrogen sulphide was taken to have the higher calorific value of 630 B.t.u. per cu. ft. at 60° F. and 30 in. of mercury as given in works of reference. The lower calorific value was then 581 B.t.u. per cu. ft. in the standard conditions of temperature and pressure and was used for calculations of thermal efficiency.

The engine trials were run at 12 : 1 compression ratio, an engine speed of 900 r.p.m. and with the jacket coolant at 212° F. Although data were available for a trial made earlier when using town gas in the conditions mentioned, there was some uncertainty about the condition of surfaces in the combustion space, the engine not having been dismantled for cleaning since the beginning, some three months earlier, of the trials with town gas described in Part XIII (7). It was planned, therefore, to run a new trial with town gas, after cleaning the combustion space by means of a brush and scraper inserted through the spark plug and bouncing pin holes; a great deal of surface area could not be reached in this way. The trial was then to be followed by one with the addition of hydrogen sulphide to the gas–air mixture.

The trial with town gas alone was begun on Sept. 8, 1949, but was discontinued because dust from concrete work in progress nearby the engine induced

knocking combustion. A similar proknock effect had been obtained from concrete dust a year earlier when hydrogen was being used as the fuel for the same engine (9).

The work was resumed the next day, the dust concentration in the laboratory atmosphere having become normal, and the two trials were completed during the period 7 a.m. to 11 p.m. Measurements were made of brake and indicated horsepower and of rates of air and gas supply. Optimum spark advance as determined by prior experiments was always used. The experimental results are given by the graphs of Figs. 1 to 3.

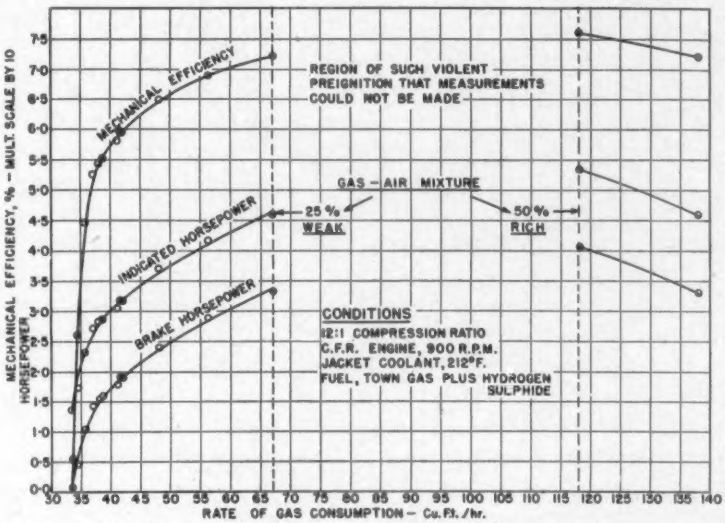

FIG. 1. *Observed values of indicated horsepower and mechanical efficiency corresponding to rate of gas consumption.*

Brake horsepower, indicated horsepower, and mechanical efficiency plotted on a base of rate of supply of town gas plus hydrogen sulphide are given by the graphs of Fig. 1. It will be noted that at rates of gas supply from 67 to 117 cu. ft. per hr. preignition was so violent that measurements of power could not be made, and it was unsafe to try to continue running the engine. Measurements were possible only at very weak or very rich gas–air mixtures as shown by the graphs.

Horsepower and mechanical efficiency measurements plotted on a base of air-to-gas ratio by volume and mixture strength percentages are shown by the graphs of Fig. 2. The value of the correct air–gas ratio shown on the figure as approximately 4.25 is the mean of values with and without hydrogen sulphide, which possesses a higher calorific value than the town gas. It will be noted that the mixture strength region over which operation of the engine

was prevented by preignition was from 25% weak to 50% rich. Preignition was pronounced even with the mixture 25% weak but was not sufficiently severe to prevent measurement.

It is not necessary to give in detail the results of the trial made when using town gas alone. They confirmed those obtained earlier in the same conditions which are shown by the graphs of Figs. 3 and 3, *A*, Part XIII (7), except

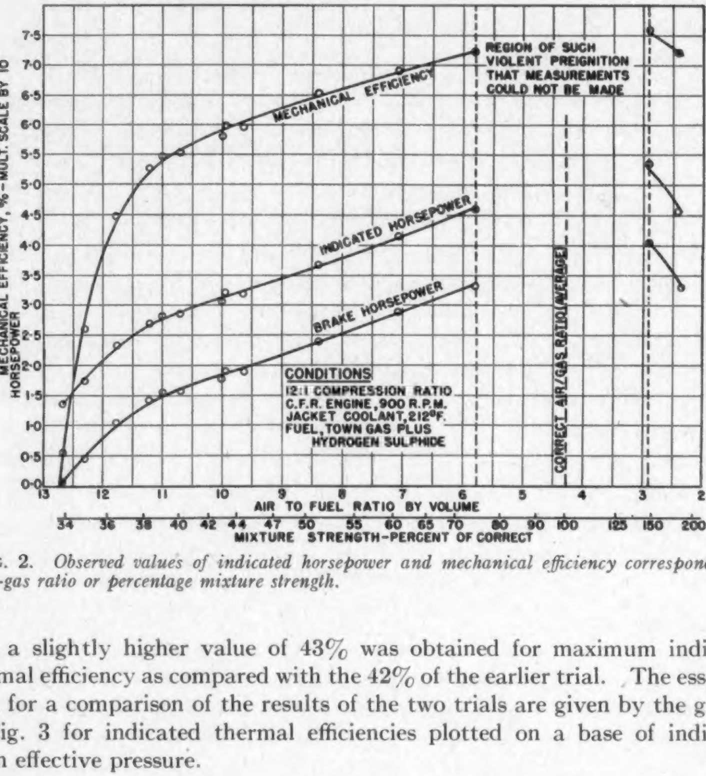

FIG. 2. *Observed values of indicated horsepower and mechanical efficiency corresponding to air-to-gas ratio or percentage mixture strength.*

that a slightly higher value of 43% was obtained for maximum indicated thermal efficiency as compared with the 42% of the earlier trial. The essential data for a comparison of the results of the two trials are given by the graphs of Fig. 3 for indicated thermal efficiencies plotted on a base of indicated mean effective pressure.

It will be seen by reference to the graphs that a maximum value of 44% was obtained for indicated thermal efficiency when the gas–air mixture contained hydrogen sulphide. This is an increase of 2.3% on the value obtained without hydrogen sulphide during the trial made earlier the same day and an increase of 4.8% on the value obtained for the trial described in Part XIII (7) when using a jacket coolant at 212° F. Maximum indicated thermal efficiency was obtained at about half power with a gas–air mixture 50% weak. On going to still weaker mixtures the value was progressively less affected by the hydrogen sulphide.

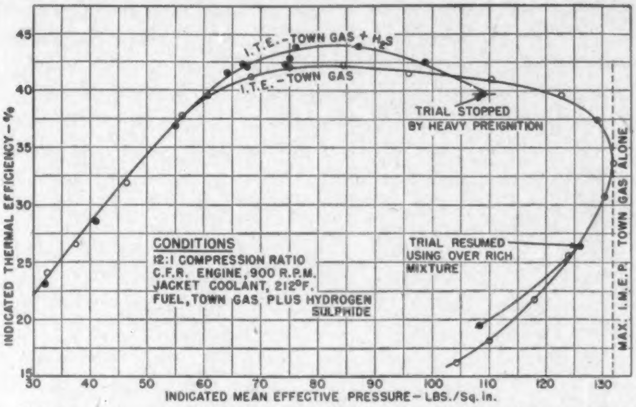

FIG. 3. *Relation between indicated thermal efficiency and indicated mean effective pressure with and without hydrogen sulphide in gas–air mixture.*

Preignition developed almost immediately on going to richer mixtures. Thermal efficiency diminished at a relatively high rate and preignition became so violent when values of the I.M.E.P. exceeded 109 lb. per sq. in. that measurements could not be made. The mixture strength was then increased to be 50% rich. Preignition did not occur and measurements could again be made.

The Residual Sulphur Effect

The experiments made with sulphur added to liquid fuels, described in Part III (5), disclosed the existence of a marked residual effect. It persisted even after the usual thorough cleaning of the combustion chamber surfaces with the engine dismantled and caused knocking combustion even when benzene was used at moderate compression ratios. The knocking combustion did not stop until after the engine had again been dismantled and the combustion chamber surfaces given a second and more drastic cleaning.

It was expected accordingly that a similar residual effect might exist after using town gas plus hydrogen sulphide even for the relatively short time of about five hours taken for the experiments described in this Part. The existence of the effect was verified by experiments. The engine was then dismantled and the combustion chamber surfaces drastically cleaned, special attention being given to the piston crown and the exhaust valve. Some residual effect was observed on again using the engine, and a period of 70 hr. running on a weak pentane–air mixture was required before the standard knock intensity corresponding to a particular octane–heptane mixture was regained.

Discussion

It was shown by experiments described in Part III (5, pp. 137-139) that a pentane–air mixture in combining proportions, passing through a red hot, 670° C., 1238° F., steel combustion tube would not ignite and explode because

of the reduction of its inflammability by dilution with the steam and carbon dioxide formed by surface oxidation. If, however, hydrogen sulphide were added to the pentane–air mixture, ignition and explosion occurred at 580° C., a temperature corresponding to less than a dull red heat. It is well known that in the circumstances the effect of the hydrogen sulphide is to convert the surface of the steel tube to iron sulphide which is inactive to oxidize hydrocarbons to steam and carbon dioxide or hydrogen to steam.

It was shown further by experiments described in the reference quoted that the surface effect to inhibit oxidation to steam and carbon dioxide remained when the hydrogen sulphide was no longer added to the pentane–air mixture, explosion then occurring at a temperature 10° C. only higher than when the hydrogen sulphide was present in the mixture. The residual effect supports the view that neither the inhibitory action of hydrogen sulphide on the reaction to steam and carbon dioxide nor the reaction itself is other than a surface effect. Furthermore, it may be concluded that the degree of the inhibitory effect depends on time of exposure of the steel surface to the action of hydrogen sulphide as well as to the concentration of that "catalytic poison" in the combustible mixture.

The effect of steam formed by the oxidation of *hydrogen* in mixtures with air, on a surface of iron oxide to raise the ignition temperature, is shown by experiments also described in Part III (5, p. 128). Thus on passing the mixture through a silica tube, rate of oxidation of the hydrogen to steam was just measurable at 550° C. and explosion occurred at 587° C. When, however, the surface of the tube became partly coated with iron oxide, the hydrogen oxidized to steam with great rapidity and a temperature of 667° C. was required for ignition.

It will be noted that the igniting temperature of 587° C. for hydrogen in contact with an inactive silica surface is nearly the same as that of 590° C. for a pentane–air mixture on a steel surface made inactive by the poisoning effect of hydrogen sulphide.

The effect of surface reactions occurring when town gas is used in an engine can now be described. The principal constituents of the gas are hydrogen, carbon monoxide, and methane, and in the Toronto variety the approximate percentage concentrations are 50, 22, and 12 respectively. The average igniting temperatures of the gases in mixtures with air, given by Coward (3) as having been determined by H. B. Dixon when using a combustion tube having an inactive, porcelain, surface are, hydrogen 585° C., carbon monoxide 650° C., and methane 700° C. Therefore hydrogen, having the lowest surface ignition temperature and forming by far the largest constituent of town gas, would be expected to be responsible for preignition when it occurs in gas engines, a view in accordance with statements made in textbooks. The view is correct solely if the surfaces in the combustion space are *inactive* to oxidize the hydrogen to steam. *Active* surfaces can be raised to temperatures

higher than a red heat without igniting hydrogen–air mixtures in contact with them as illustrated by the graphs of Fig. 4. The graphs give the igniting temperatures for hydrogen–air mixtures passing through silica and stainless steel combustion tubes and are selected from experimental results obtained by King and Mole (8). Ignition occurred in the silica tube at a temperature as low as 565° C. It was not greatly affected by the concentration of hydrogen in the mixture which in the conditions was inflammable for contrations varying from 5 to 90%. The minimum igniting temperature of the mixture in contact with the steel surface was 630° and mixtures containing hydrogen in concentrations less than 20% or greater than 30% could not be ignited even at the measurable maximum of 750°C.

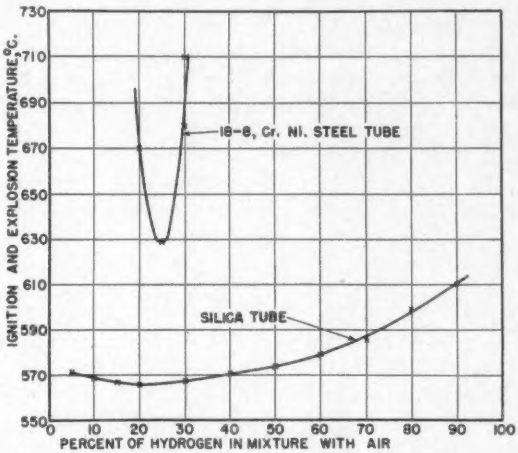

FIG. 4. *Igniting temperatures and range of inflammability of hydrogen–air mixtures passing through open combustion tubes 1 in. internal diameter. Mixtures supplied at the rate of 150 cc. per min.*

The conclusion is that the hydrogen constituent of a fuel gas is of useful effect to prevent preignition but of evil effect if the combustion chamber surfaces are such that oxidation thereon of the gas to steam cannot occur. Initially clean steel or iron surfaces in the combustion space become coated with metallic oxide almost immediately on running the engine under power. Steam is formed on the reduction of the oxide by the hydrogen, and compression ratio can be raised to values even higher than the 12 : 1 used for the trials of this Part, without the occurrence of preignition or detonation. The steam not only prevents preignition by hot surfaces but by reducing the inflammability of the end gas counteracts the igniting effect of finely divided carbon derived from pyrolysis of the lubricating oil to promote detonation. The steam forming reaction is continuous because in equilibrium conditions the rate of reduction of the oxide by hydrogen is equal to the rate of oxide formation by the oxygen in the gas–air mixture. The evil effect of hydrogen

becomes apparent when the surface reaction to form steam is inhibited by hydrogen sulphide because the surface ignition temperature of hydrogen then becomes lower than that of the other gases present in appreciable proportion in town gas.

All of the above mentioned effects are exemplified by the experiments of this Part made with combustion chamber surface temperature rising from that corresponding to zero brake horsepower to that attained at maximum power and then decreasing as power decreases with the use of overrich mixtures. Refer now to Fig. 3, and follow the graphs beginning with the minimum I.M.E.P. of 30 lb. per sq. in. for which brake horsepower is zero. It will be seen that indicated thermal efficiency values remain the same with and without hydrogen sulphide in the gaseous mixture until I.M.E.P. exceeds 60 lb. per sq. in. That is, the heat developed over the low power range is insufficient to raise surface temperature to the degree required for the oxidation of hydrogen to steam at an appreciable rate. There is then no reaction to be inhibited by the hydrogen sulphide and it provides merely part of the heat value of the combustible mixture, taken into account in calculating thermal efficiency.

The graphs diverge at the surface temperature attained when power exceeds 60 lb. per sq. in. I.M.E.P., indicating that rate of surface oxidation of the hydrogen to steam has become appreciable because thermal efficiency rises when the reaction is inhibited by the poisoning effect of the hydrogen sulphide.

The maximum value of the thermal efficiency attained on inhibiting the steam forming reaction is 44% as compared with the average maximum of 42.5% obtained otherwise. The maximum values were however always obtained for mixtures 50% weak and at corresponding surface temperatures. On using richer mixtures to increase power and consequently surface temperature, preignition became noticeable for the mixtures containing hydrogen sulphide and so heavy when I.M.E.P. exceeded 109 lb. per sq. in. that it was necessary to stop the engine. It was possible, however, to resume the trial at the lower surface temperature corresponding to a mixture 50% rich and to obtain then a slight increase of indicated thermal efficiency with hydrogen sulphide in the gaseous mixture, presumably because then the beneficial effect of inhibiting steam formation can be realized without the incidence of preignition, just as occurred when weak mixtures were used.

Concluding Comment

The experiments of this Part and those of Parts XII (6) and XIII (7) demonstrate that the hydrogen content of fuel gas free of sulphur renders it possible to run a gas engine at Diesel engine compression ratios, but at the expense of some slight loss of possible thermal efficiency. Thus the maximum thermal efficiency obtained at 10 : 1 compression ratio, Part XII, was 41% which is 68.5% of the air standard value of 59.8%. The maximum value

(average) of the trials made at 12 : 1, Part XIII and this Part, was 42.5% which is 67.9% of the corresponding air standard value of 62.6%. When the gaseous mixture contained hydrogen sulphide and the steam forming surface reaction was inhibited, maximum thermal efficiency rose to 44% which is 70.3% of the air standard value.

Maximum thermal efficiency is however obtained for a gas–air mixture 50% weak. As the mixture is enriched to increase power and consequently surface temperature, the formation of steam by surface reaction becomes increasingly necessary for the prevention of preignition. Without the steam forming reaction, which is made possible by the hydrogen content of the fuel gas, the engine can be run at high compression ratios on light loads only.

The concentration of sulphur in fuel gas required to prevent the use of high compression ratios as mixture strength and power are increased from relatively low values has not been determined. The concentration of 10 to 15 grains of organic sulphur in Toronto town gas seemed to be without ill effect. The degree of concentration is probably of little importance because of the residual effect. Thus a small concentration, but exceeding a possible threshold value, used for a long period would be expected to have the same poisoning effect on the surface as a larger concentration used for a short one.

The experiments described in this Part have been solely those showing that it is the *combined* effect of hydrogen and hydrogen sulphide which limits the use of fuel gases containing hydrogen in large proportion to the compression ratios of from 5 to 5.6 : 1 currently used in practice. The *combination* is of evil effect also in respect of cylinder wear. Thus Broeze and Gravesteyn (1) conclude that, at the high temperatures and pressures attained in the combustion space of Diesel engines, sulphur trioxide, rather than the dioxide, is formed and that the sulphuric acid arising from reaction of the trioxide with steam can account for a high rate of cylinder wear.

A further sulphur effect not dealt with in this Part is the proknock action of certain of the compounds arising from nuclear ignition of the end gas on their decomposition to finely divided sulphur. It is to be noted also that the use of so high a compression ratio as 12 : 1 for town gas free of sulphur is possible if the air supply does not contain an unusual concentration of dust and if the lubricating oil does not decompose to yield sufficient finely divided carbon for nuclear ignition.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, and Assistant Prof. W. A. Wallace. Mr. J. Alex. Morrison, supervisor of the appliance laboratory of the Consumers' Gas Company, Toronto, assisted by supplying necessary data in respect of the town gas used for the trials and newly calibrated special gas meters. Mr. S. Sandler

of Defence Research Board Fuels Laboratory in the Department of Chemical Engineering, University of Toronto, was responsible for the supply and measurement of additions of hydrogen sulphide to the town gas used for the engine trials.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XV. THE CONCENTRATION OF FINELY DIVIDED CARBON IN TOWN GAS-AIR MIXTURES REQUIRED TO INDUCE SEVERE KNOCKING COMBUSTION[1]

By R. O. King[2], E. J. Durand[3], and A. B. Allan[4]

Abstract

When using gaseous fuels for the C.F.R. engine, the lubricating oil decomposed to finely divided carbon when the gas was hydrogen and optimum spark advance nearly zero. When town gas was used, optimum spark advance varied from 85 to 15 degrees of crank angle, according to mixture strength, and the lubricant yielded carbon of the hard adherent graphitic variety. When using an L head engine having a combustion chamber with a large surface-to-volume ratio and with the spark plug so placed that optimum spark advance for town gas was approximately half that required with the C.F.R. engine, no appreciable carbon deposit of any variety was obtained. Conditions were therefore such that knocking combustion observed on adding finely divided carbon to the gas–air mixture was not caused to any appreciable degree by carbon derived from the lubricant. It was then found on adding carbon, as graphite dust, at a measured rate to the entering mixture, that approximately 0.3 mgm. in the end gas caused a knock intensity of the degree required to reduce brake horsepower by from 10 to 14%.

Introduction

The experiments described in this Part were made in the course of an investigation of the factors which have hitherto prevented the use of fuel gases in Otto cycle spark ignition engines at other than economically low compression ratios. The experiments deal especially with nuclear ignition which is of interest in respect of the ignition and explosion, in any circumstances, of mixtures of air with combustible gases or vapors.

The investigation was begun with hydrogen and experiments, Part V (4), demonstrated that the gas could be used in any proportion in mixtures with air at a compression ratio as high as 10 : 1 if it were not impregnated with finely divided carbon derived from pyrolysis of the lubricating oil. It was expected, therefore, that finely divided carbon would be formed when town gas containing hydrogen in a concentration of nearly 50% was used in the engine and that consequent nuclear ignition would again be obtained. It was found, however, as a result of experiments made accordingly and described in Parts XII (2) and XIII (3), that the carbon residue in the combustion chamber was of the hard and adherent graphitic type. There was little if any evidence of the finely divided variety having been formed and a compression ratio of 12 : 1 was used without the occurrence of nuclear ignition.

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Contribution from the Defence Research Board (Canada), in association with the Department of Mechanical Engineering, University of Toronto, Toronto, Ont.

[2] *Research Scientist, Defence Research Board, Ottawa, Canada.*
[3] *Lecturer, Department of Mechanical Engineering, University of Toronto.*
[4] *Research Assistant, Department of Mechanical Engineering, University of Toronto.*

The further experiments described in this Part were made with the Armstrong–Whitworth knock testing engine (1) and the results differed from those obtained with the C.F.R. engine in that no appreciable amount of carbon of any variety remained in the combustion chamber.

The experimental results are interpreted as showing why the oil used to lubricate the pistons of internal combustion engines may or may not leave a carbonaceous deposit in the combustion chamber and why a deposit may be of the finely divided or the adherent graphitic type.

The conditions in which the lubricating oil left no carbon in the combustion space having been ascertained, it became possible on adding finely divided carbon to the gas–air mixture at a measured rate to determine the concentration required to cause nuclear ignition and consequent combustion knock of the intensity required to reduce power by a measurable amount.

Experimental Arrangements and Methods

The Engine

A desirable feature of the Armstrong-Whitworth engine is that the detachable head facilitates the inspection or removal of carbonaceous or other deposits that may have collected in the combustion chamber or adhered to the surfaces. The disadvantages of the engine are that the maximum designed compression ratio is 8 :1 only and that the attainable mean effective pressure is low as compared with that of the C.F.R. engine.

The essential features of the combustion chamber are illustrated by Fig. 1. The plunger *P* is adjustable by a screw to vary compression ratio over the

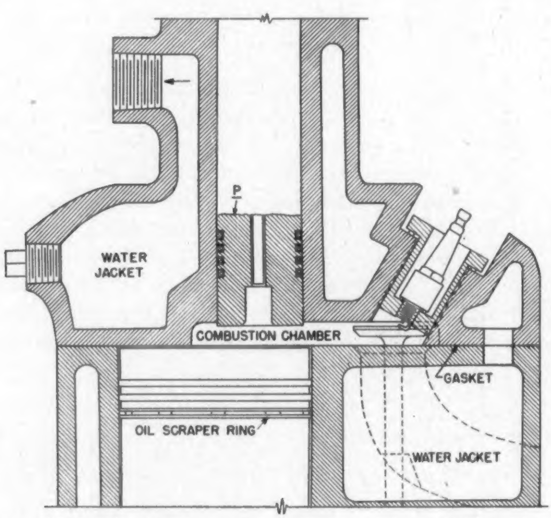

FIG. 1. *Combustion chamber arrangements—Armstrong–Whitworth engine.*

range 4 to 8 : 1. The higher value of 9 : 1 used for the experiments presently described was obtained by lowering the plunger to project 1/8 in. into the combustion space, by reducing the volume of the spark plug hole, and by using an extra-thin, 1/64 in. asbestos composition cylinder head gasket.

The cylinder diameter is 2 7/8 in., the stroke 3 1/2 in., and the stroke volume 22.7 cu. in. The engine and a direct connected swinging field electric dynamometer are mounted as a unit on a cast iron bedplate. The engine was designed originally for the knock rating of fuels but became obsolete on the universal adoption of the C.F.R. engine for that purpose.

Lubrication and Carbon Deposits

It was necessary for the experiments that excess lubricating oil should not pass the piston and that the cylinder head gasket should be tight enough to prevent water or steam entering the combustion space. Some difficulty was experienced in overcoming the evils. The oil difficulty disappeared on replacing the lowest of the three pressure rings by an effective scraper ring fitted in a groove widened from 0.125 in. to 0.140 in. to receive it and on replacing the remaining pressure rings by new ones of a superior design. Water leakage was stopped, in spite of the extremely thin gasket, by scraping the surfaces of the cylinder head and block to an approximate surface plate flatness.

Method of Admitting Finely Divided Carbon, as Graphite Dust

Mechanical methods were tried, beginning with a screw feed stoker design as mentioned in Part V (4). All were defective for the principal reason that induction oscillations made it difficult to govern the rate of feed by mechanical means. It was decided finally to make use of the oscillations to assist in picking up and feeding the dust into the combustion chamber. The device

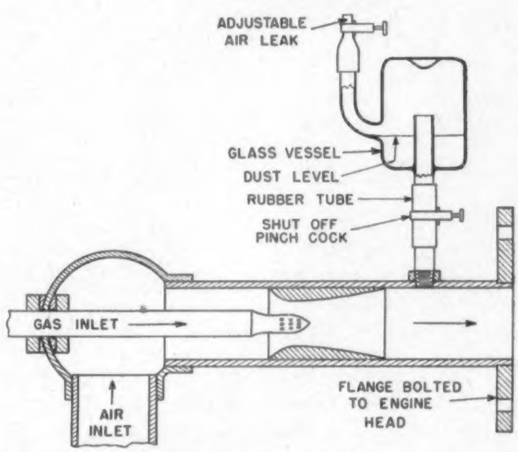

FIG. 2. *Device for adding graphite dust to the gas–air mixture.*

used was fitted to the induction pipe between the carburetor and the engine head as illustrated by Fig. 2. It comprises a glass vessel with a central standpipe for the admission of the oscillations from the induction pipe and a filling tube at one side. The device is set in operation by fully opening the lower pinchcock, and the rate at which dust is picked up and carried into the combustion chamber can be varied by adjusting the pinchcock at the top of the side tube to provide a small air leak. The vessel is filled with dust to the level shown by the illustration before taking an observation, and the air oscillations act to remove dust at a rate depending on the size of the air leak. The rate is substantially uniform if not more than a total depth of about 1/8 in. of dust is removed before refilling. The vessel can be refilled without altering the size of the air leak. The regularity of the action is no doubt due to the magnitude of the oscillation remaining constant when the engine speed is unchanged, and the mixture supplied at constant pressure, no throttle being used.

Particulars of Toronto Town Gas

Analysis of Toronto town gas is carried on continuously by the Consumers' Gas Company. The composition determined at the time of the experiments is given below,—

TABLE I

Composition of Toronto Town Gas

Constituents	Percentage volume
Hydrogen	47.5
Carbon monoxide	21.3
Methane	12.3
Nitrogen	7.8
Carbon dioxide	4.6
Ethylene	3.9
Ethane	1.1
Benzene	1.0
Oxygen	0.5

The gas contains a trace of organic sulphur not exceeding 10 to 15 grains per 100 cu. ft.

Hydrocarbons constitute a relatively small proportion of the gas and with the exception of the ethylene present in very small concentration are of the type to resist pyrolysis to finely divided carbon even at the temperature of the end gas, that is, they are of the nonknocking variety.

The higher calorific value determined by calorimeter in the Gas Company Laboratory was 467 B.t.u. per cu. ft. at 60° F. and 30 in. of mercury. The lower value, by calculation, was 424 B.T.U. per cubic foot and the density 0.0409 lb. per cubic foot.

The rate of gas supply to the engine was measured by a standard dry meter fitted with a special dial for accurate reading and calibrated by the Consumers' Gas Company.

Experimental Results

Performance Data for the Armstrong–Whitworth (A-W) and C.F.R. engines

Performance data for the two engines were obtained by trials in like conditions for the purpose of facilitating comparison of later experimental results. The trial conditions were, speed 800 r.p.m., jacket coolant 212° F., air and gas at laboratory temperature, and compression ratio 9 : 1.

The value assigned to the compression ratio is based on a measurement of the clearance volume, but even if measurement be correct the *compression pressure* will be less than the correct corresponding value to an extent depending mainly on the amount of leakage past the piston, valves, and cylinder head gasket. The maximum compression pressure for the A–W engine in the conditions mentioned above, taken immediately after running under power, was 207.5 lb. per sq. in. when atmospheric temperature was 85.8° F. and pressure 29.69 in. of mercury. The comparable compression pressure

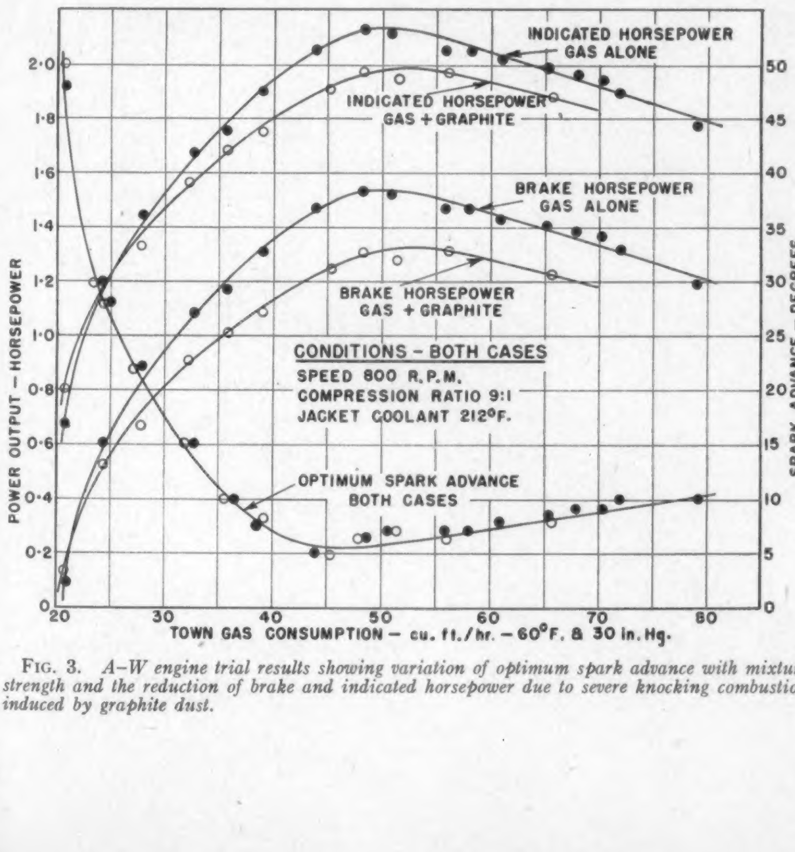

FIG. 3. *A–W engine trial results showing variation of optimum spark advance with mixture strength and the reduction of brake and indicated horsepower due to severe knocking combustion induced by graphite dust.*

for the C.F.R. engine was 209.0 lb. per sq. in. when atmospheric temperature was 82.5 °F. and pressure 29.8 in. of mercury. The small difference of 1.5 lb. per sq. in. in favor of the C.F.R. engine can be accounted for in part by the lower atmospheric temperature and higher pressure and in part by the piston being fitted with three pressure rings instead of the two of the A–W engine. Moreover, there is always a possibility of leakage past the cylinder head gasket of that engine, whereas the C.F.R. engine is constructed with the cylinder head and barrel in one piece, and a jointing gasket is not required.

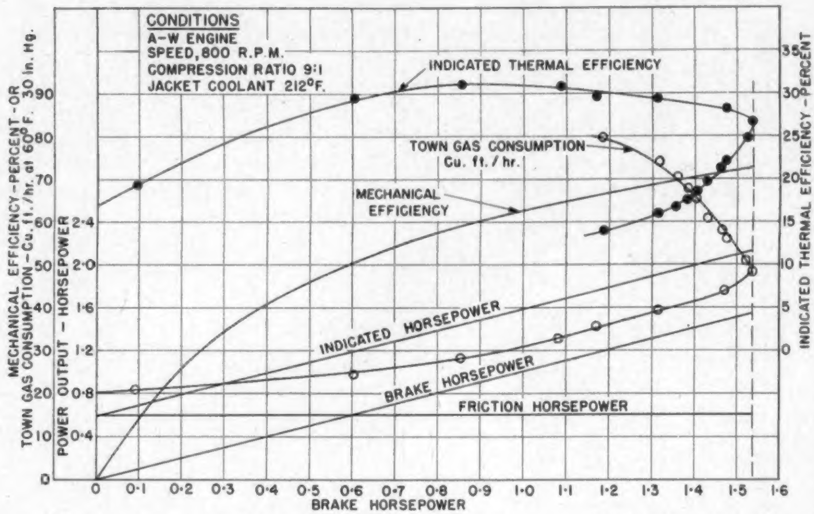

FIG. 4. *A–W engine trial; collected results showing especially that indicated thermal efficiency reaches a maximum at 55% of full load and then diminishes as mixture strength is weakened to reduce power.*

Performance data for the A–W engine are given in some detail by the graphs of Figs. 3 and 4. The similar data for the C.F.R. engine need not be given in detail, the essential difference between the performances of the two engines being shown by the graphs of Fig. 5. They show that indicated mean effective pressure for the C.F.R. engine attained a value of 126 lb. per sq. in., the corresponding indicated thermal efficiency being 33%. The similar values for the A–W engine were 92 lb. per sq. in. and 27%. The indicated thermal efficiencies attained at the mixture strengths for maximum economy were 39.5% for the C.F.R. and 31.0% for the A–W engine.

The inferior performance of the A–W engine is attributed, in accordance with experiments made by Ricardo (6, p. 203), to the relatively large surface-to-volume ratio of the combustion chamber. The ratio is usually calculated on the basis of the piston being at top dead center. The effective ratio is however that calculated for the position of the piston when combustion is

appreciable. That would be at about 10 crankshaft degrees after passage of the spark. On this basis the surface-to-volume ratio is 7.6 for the A–W and 3.1 for the C.F.R. engine, the ratios being taken for piston positions at maximum thermal efficiency when spark advance is 50° for the C.F.R. and 32° for the A–W engine.

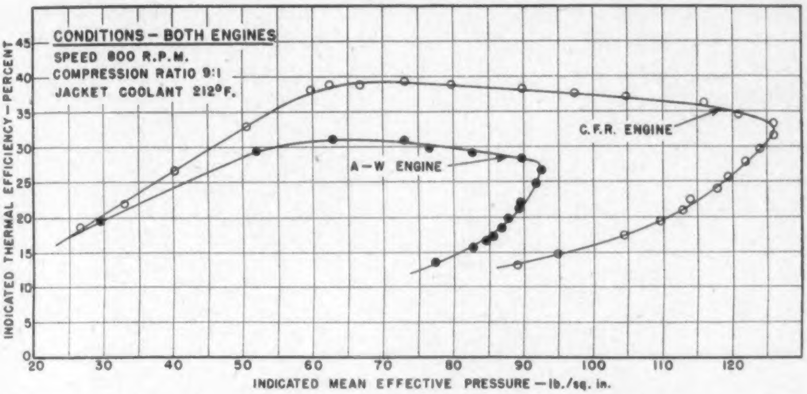

FIG. 5. *Relative performances in terms of indicated thermal efficiencies and mean effective pressures of the C.F.R. overhead valve engine and the A–W, L head side valve engine.*

Spark Plug Position and Optimum Ignition Timing

Optimum ignition timing varies with mixture strength and was determined by a separate series of experiments as described in Part XII (2, p. 438). The values so obtained for the A–W engine as given graphially, Fig. 3, are much less than values obtained similarly for the C.F.R. engine. At maximum power, optimum ignition timing required a spark advance of 7° for the A–W and 15° for the C.F.R. engine. At minimum power, zero *brake* horsepower, optimum ignition timing for the A–W was 50° spark advance and 85° for the C.F.R. engine. The somewhat remarkable difference is attributed to the difference in spark plug position. The spark plug of the A–W engine is situated between the side-by-side inlet and exhaust valves and close to them. Thus the spark passes and flame propagation begins in what is substantially freshly admitted combustible mixture that has been heated by contact with the exhaust valve as well as by compression. The spark plug of the C.F.R. engine is situated as far as space permits from the inlet and exhaust valves which are as widely separated as space permits. Thus on the passage of the spark, flame propagation must occur in a mixture diluted to the maximum possible extent with residual exhaust gas, consequently an unusually large advance is required for optimum ignition timing, especially when weak mixtures are used. The attainment of 100% quality control when using the standard ignition system is attributed to the advantageous position of the spark plug.

Combustion Chamber Cleanliness

It was of importance to determine if the experimental arrangements were effective to prevent the accumulation of loose carbon in the combustion space. A trial was run accordingly at maximum power for a period of 92 hr., not continuously. The lubricant was composed of commercial acid-refined hydrocarbon oils blended in the laboratory to provide an S.A.E. 30, viscosity grade. The engine ran for the period without developing combustion knock, and occasional inspection made after removing the engine head showed that carbon was not accumulating in the combustion chamber. At the end of the 92 hr. running time there was a trace only of adherent carbon as a narrow ring around the periphery of the piston and a corresponding faint ring of adherent carbon on the flat part of the head adjacent to it at top dead center. The faint ring of carbon was no doubt due to oil thrown from the edge of the piston as the motion reversed at top dead center. There was also a slight deposit of adherent carbon adjacent to the inlet valve. Otherwise the chamber was clean.

Rate of Admission of Graphite Dust and Consequent Knock Intensity

Graphite instead of carbon dust was used for the experiments, in the expectation, based on earlier experiments, that it would be the more likely to remain dispersed in the gaseous mixture instead of clinging to surfaces and accumulating in the combustion chamber.

The graphite dust, grade No. 2301, was supplied by the Canadian National Carbon Company Limited and consisted of a mixture of "impapable" powder and larger particles that had passed through a 200 mesh to the inch sieve. The grade is that commonly used in iron foundries for dusting on green sand molds.

Knock intensity is a relative term and the C.F.R.–A.S.T.M. method of defining it in terms of the Octane Scale is unsuitable for use with a non-knocking fuel such as town gas, and a practicable method seemed to be to admit the graphite dust at a constant rate and to determine the consequent degree of knocking combustion in terms of the resulting drop in power and thermal efficiency. What can be described in general terms as steady severely hard knock was obtained when the graphite dust was admitted at the rate of 1.3 oz. per hr. which at the engine speed of 800 r.p.m. is 1.5 mgm. per induction stroke.

The engine performance in terms of brake and indicated horsepower is shown by the graphs of Fig. 3 for gas alone and for gas plus graphite dust admitted at the rate mentioned. The severe knocking combustion induced on adding the dust was accompanied by a decrease in B.H.P. of from 1.54 to 1.32, or 14%, and an increase in gas consumption of from 50 to 53 cu. ft. per hr.

Effect of the Knocking Combustion on Thermal Efficiency

Indicated and brake thermal efficiencies based on the lower heating value (L.H.V.) of 424 B.t.u. per cu. ft. at 60° F. and 30 in. of mercury for the town gas are given by the graphs of Fig. 6. The graphs showing efficiencies when

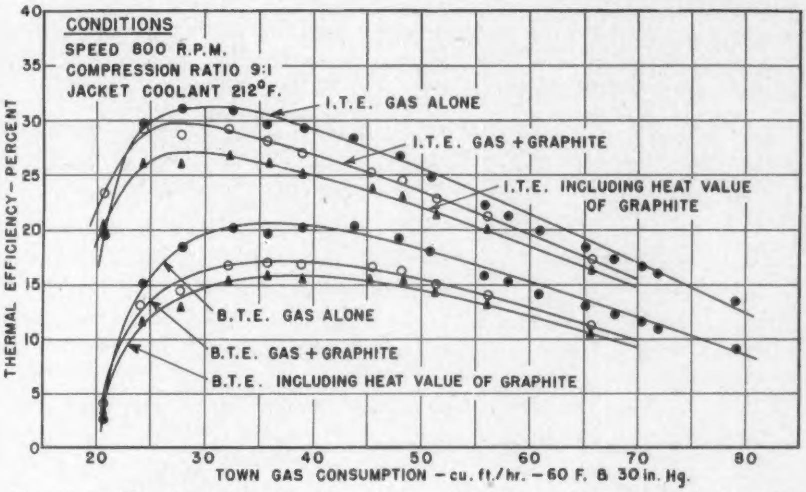

FIG. 6. *A–W engine trial; effect of knocking combustion caused by graphite dust to reduce indicated and brake thermal efficiencies.*

the heat of combustion of the graphite is taken into account are based on the assumption that it is used with the same thermal efficiency as the town gas. The values shown by the graphs are probably too low because it is doubtful that complete combustion of the graphite occurs when the heat developed can be used with maximum efficiency.

Discussion

It is of interest in respect of the nuclear ignition of gaseous fuels to determine the conditions in which lubricating oil will decompose to the finely divided carbon required to cause the effect.

The absence of finely divided carbon in the combustion space of the A–W engine cannot be attributed to acid-refined oil having been used because a similar result was obtained on using a high grade solvent refined oil or a nonhydrocarbon base synthetic oil for equally long periods of running. It remains, therefore, to consider the combustion conditions in which the finely divided carbon is or is not formed.

When hydrogen alone was used as the fuel for the C.F.R. engine a deposit of fluffy carbon having the appearance of lampblack built up in a few hours

running with the effect of igniting the hydrogen–air mixture; Part V (4). The engine was lubricated with a solvent refined oil.

When town gas alone was used in the C.F.R. engine, the residue from the solvent refined oil was the hard graphitic type of carbon, and nuclear ignition was not obtained even at a compression ratio of 12 : 1, Part XIII (3). When town gas was used alone as the fuel for the A–W engine, there was no residue of finely divided carbon in the combustion space and an almost inappreciable amount of the adherent variety, even after 50 hr. running.

The variable factors affecting combustion in the engines were spark advance and the surface-to-volume ratios of the combustion chambers of the C.F.R. and the A–W engines. The effect of these factors on carbon formation will now be discussed.

Spark advance determines the time of exposure of the oil film on the combustion chamber surface to the destructive effect of flame temperature. The effect over a period of time would result not only in the drastic decomposition of the oil to carbon and hydrogen but in at least partial conversion of the carbon to graphite. When hydrogen was used as the engine fuel, combustion occurred in a few degrees of crank angle and in some cases optimum spark advance was negative, i.e., the mixture with air was ignited after top dead center. It was solely in these combustion conditions that finely divided carbon was found in the combustion chamber.

Combustion conditions were very different when town gas was used as the fuel for the C.F.R. engine. Then optimum spark advance varied from 85 to 15 degrees of crank angle and the oil film was exposed to the destructive effect of the flame for a period many times greater than when hydrogen was used as the fuel. It was in these conditions that the hard adherent graphitic type of carbon was formed.

When the town gas was used in the A–W engine, optimum spark advance varied from 50 to 7 degrees of crank angle and time of exposure of the oil film to flame temperature was approximately half of that in the C.F.R. engine. Furthermore, the relatively large surface-to-volume ratio of the combustion chamber of the A–W engine ensured a lower surface temperature than prevailed in the C.F.R. engine. That is, conditions were such that the lubricating oil could distill off the surface instead of being decomposed to carbon. In any event, conditions in the combustion space of the A–W engine were such that the knocking combustion obtained on adding graphite dust to the gas–air mixture was not caused to any appreciable degree by finely divided carbon derived from pyrolysis of the lubricating oil.

The concentration of 1.5 mgm. of graphite dust per stroke volume shown by the experiments to be required to induce severe knocking in the A–W engine at 9 : 1 compression ratio is equivalent to a concentration of 180 grains per 100 cu. ft. of air at atmospheric pressure. This is a high value

considering that 8 grains per 100 cu. ft. is regarded as a high concentration in a dusty mine (5, p. 1878). It was far in excess of that required for audible knock and was used, as already mentioned, in order to obtain a consequent measurable decrease of power.

The extreme difference between audible knock and the degree used for the experiments, in terms of compression ratio and B.H.P., is illustrated by the graph of Fig. 7, for an experiment with the C.F.R. engine made when

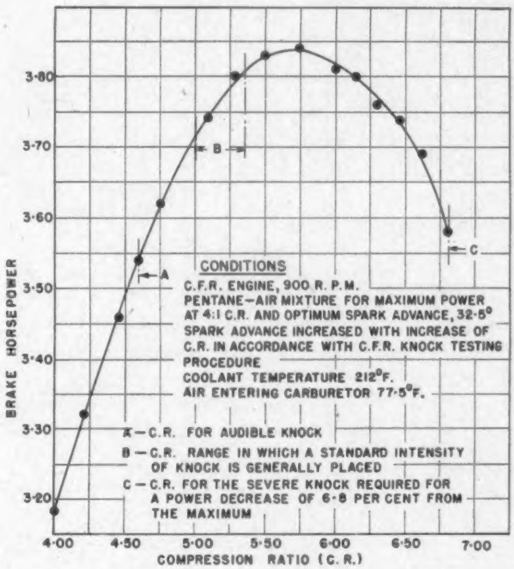

FIG. 7. *Graph showing the range of power and compression ratio possible with knock intensity varying from audible to severe.*

using *n*-pentane as the fuel. It will be seen that audible knock occurred at a compression ratio of 4.6 : 1; the B.H.P. being then 3.54. The compression ratio could then be raised to 5.27 with a corresponding increase of B.H.P. to 3.8 while the knock intensity did not increase to exceed that commonly used as "standard" and greater intensity could be obtained by raising the compression ratio to 5.62 : 1 before power began to diminish. A still greater knock intensity obtained by raising the compression ratio to 6.8 was required to cause a 9% decrease in power.

Knocking combustion, due to nuclear ignition, requires a suitable concentration of finely divided material in the end gas only. The concentration can be provided accordingly when using hydrocarbon fuels because the decomposition reaction required to provide finely divided carbon can occur preferentially in the end gas in the temperature and pressure conditions

attained late in the combustion period. When, however, a nonknocking fuel such as town gas is used in an engine and the finely divided material added to the gas–air mixture as admitted, it is necessary to impregnate the whole mixture to the concentration required for nuclear ignition of the small part which constitutes the end gas.

It is reasonable to assume that the severe knocking combustion obtained when the gas–air mixture supplied to the A–W engine contained 180 grains of graphite dust per 100 cu. ft. occurred when combustion was 80% complete. The weight of dust in the 20% remaining to constitute the end gas would then be 0.3 mgm. at any one knocking combustion.

There seemed to be a possibility that graphite dust on being added to the gas–air mixture in sufficient concentration to cause severe knocking combustion would give rise to ignition by compression. Special experiments were made accordingly but the effect was not obtained at 9 : 1 compression ratio; jacket coolant being at 212° F., engine speed 800 r.p.m., and the gas–air mixture supplied at room temperature.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, and Assistant Professor W. A. Wallace. The cost of the work was defrayed in part by an extra mural grant from the Defence Research Board, Canada. The National Research Council contributed to the investigation by lending the Armstrong–Whitworth engine. The Consumers' Gas Company of Toronto contributed by lending a newly calibrated special gas meter and by supplying data for the composition and calorific value of the town gas. The Canadian National Carbon Company contributed by supplying the finely divided graphite.

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NOISE SUPPRESSION IN TRIODE AMPLIFIERS[1]

BY A. VAN DER ZIEL

Abstract

A survey is given of recent work on noise suppression in triode amplifier stages. A theory can be developed, in which the noise factor is expressed in terms of four complex quantities g_0, g_1, i_0, and i_1. g_0 and g_1 are the complex transconductances in the cathode lead and in the anode lead, respectively; i_0 and i_1 are the Fourier components of the noise currents flowing in these leads, respectively. These quantities are complex owing to transit time effects. The theory is developed under the assumption that i_0 and i_1 are completely correlated. Experiments indicate that no complete noise suppression is possible if there is no feedback; according to the above theory this means that the real part of $(g_0 - g_1 i_0/i_1)$ is positive. Knol and Versnel showed recently that a complete noise suppression can always be obtained under the above assumption of complete correlation if a suitable amount of external feedback is applied. With the help of the above theory it is shown, however, that the available power gain under those circumstances is less than unity.

1. Introduction

A few years ago it was discovered by Bakker (1) and independently by North and Ferris (4) that the spontaneous fluctuations of current emitted by the cathode of a radio tube gave rise to a noise e.m.f. in the grid circuit by electric induction. They found that this "induced grid noise" which was especially important at v.h.f. could be expressed in terms of a noise current i flowing into the grid circuit, having a mean square value:

$$\overline{i^2} = \alpha . 4kT\Delta\nu/R_{el} \tag{1}$$

in which $1/R_{el}$ is the input damping of the tube due to transit time effects (compare (4)); T is the absolute room temperature, whereas α is a constant having a value of about 5.

Equation (1) indicates that R_{el} has a high "equivalent noise temperature" αT; therefore it seems at first glance that this effect will always decrease the signal-to-noise ratio of v.h.f. circuits. Actually, however, this is not the case; induced grid noise is at least partly correlated with the shot noise of the tube and may be used to eliminate tube noise, as was first shown by Strutt and Van der Ziel (5).

Several papers have been published since; as most of them are not readily available on this continent we shall give a brief outline of their content (2, 3, 6, 8) [compare also Valley and Wallman (7)].

First consider the question of the correlation between tube noise and induced grid noise, which is the crucial point of the whole problem. It is

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Contribution from the Department of Physics, The University of British Columbia, Vancouver, B.C. Paper read at the meeting of the Royal Society of Canada, held in Halifax, N.S., on June 7, 1949.

a direct consequence of Bakker's paper (1); it also follows from the following general argument:

If an a-c. voltage is applied between cathode and grid, a current g_0V will flow in the cathode lead and a current g_1V in the anode lead (Fig. 1, (*a*), g_0 and g_1 are transconductances; owing to electron transit time effects, g_0V is delayed in phase with respect to V, and g_1V is still more delayed. Therefore a current (Fig. 1, (*b*)):

$$I = (g_0 - g_1)V = Y_eV \tag{2}$$

will flow to the grid. $Y_e = (g_0 - g_1)$ is the grid admittance due to transit time effects; its real part $1/R_{el}$ has already been introduced in Equation (1).

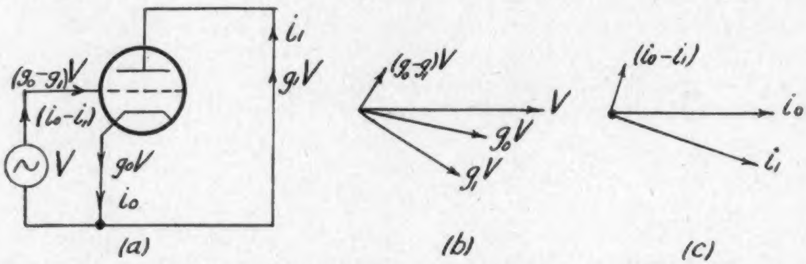

FIG. 1. (*a*) *A signal voltage V is applied to the grid of a triode; the signal currents and the noise currents in the various electrode leads are also shown.*
(*b*) *Phase relation between the applied signal voltage V, the a-c. current* g_0V *in the cathode-grid lead and the a-c. current* g_1V *in the anode lead of a triode. Owing to the phase difference between the currents* g_0V *and* g_1V *a current* $(g_0 - g_1)V$ *will flow to the grid.*
(*c*) *Phase relation between the Fourier components* i_0 *and* i_1 *of the noise currents in the cathode-grid and grid-anode lead, respectively. Owing to the phase difference between* i_0 *and* i_1 *a noise current* $(i_0 - i_1)$ *will flow to the grid.*

We now consider shot noise and apply a Fourier analysis. We denote the Fourier component of the noise current in the anode lead by i_1 and the Fourier component of the noise current in the cathode lead by i_0. In first approximation one might expect i_0 and i_1 to be completely correlated *as these Fourier components are due to the same electrons.* Owing to this correlation we may not only introduce the mean square values $\overline{i_0^2}$ and $\overline{i_1^2}$ of i_0 and i_1 but may even introduce a phase relation between i_0 and i_1 (mathematically, complete correlation means that i_0/i_1 is *not* a fluctuating quantity). Consequently a current:

$$i = (i_0 - i_1) \tag{3}$$

flows into the grid circuit; its mean square value has already been given by (1) (compare Fig. 1 (*c*))*.

**At this point it is perhaps useful to mention the symbols used in this paper. Fourier components of fluctuating quantities (instantaneous values) are denoted by such symbols as* $i_0, i_1, \ldots$ *etc. In the final analysis one is interested only in mean square values, which are denoted by* $\overline{i_0^2}, \overline{i_1^2}, \ldots$ *etc. It is a direct consequence of the Fourier analysis that one can use instantaneous values.*

We are now able to understand how a noise suppression circuit works. Introduce an impedance Z in the grid circuit; a noise voltage v will be developed across it, and this noise voltage will give rise to an additional noise current in the output lead. Z is then chosen such that this additional noise current just cancels i_1. In order to determine the value of Z, we observe that i has a phase advance of about 90 degrees with respect to i_1; a capacitive impedance $Z = 1/(j\omega C)$ between cathode and grid will give rise to a noise voltage $-i/(j\omega C)$ between cathode and grid (minus sign because i is flowing from ground to grid). This voltage has at least the required phase; by the right choice of C it will also obtain the amplitude which is necessary for the cancellation of i_1. This method of noise suppression, first suggested by Strutt and Van der Ziel (5), was experimentally verified by Kleen (2)* at 1 m. wave length. Kleen (2) used pentodes instead of triodes, therefore he could not eliminate partition noise; he could show, however, that the method worked.

The above discussion is very crude and needs refinement. In the first place one has to take into account the phase angles of the transconductances and the noise currents. In the second place one has to admit that it is impossible to make the grid impedance completely capacitive, for even with very good tuned circuits one has still to take into account the input resistance R_e of the tube which is in parallel with C. Moreover, as some input signal is required, one has to couple the grid circuit to a signal source (e.g., an antenna); the transformed internal resistance of this source is also in parallel with C. These refinements were introduced by Strutt and Van der Ziel (6), who established the conditions which a triode had to satisfy in order to make a complete noise cancellation possible. Whether or not these conditions were met in practice had to be decided by experiment.

The answer to this problem came from experiments carried out by Van der Ziel and Versnel (8). They found that for grounded-grid circuits (for which the same conditions for complete noise cancellation should hold), no complete noise cancellation could be obtained. This seemed to settle the question for a complete noise cancellation.

Recently, however, Knol and Versnel (3) showed experimentally* that, at 7 m. wave length, in a grounded cathode circuit a practically complete noise suppression could be obtained by introducing the proper amount of capacitive feedback, whereas a power gain still could be obtained at that frequency.

It is the aim of this paper to show how the single assumption of a complete correlation between i_0 and i_1 is sufficient to solve the problem of noise suppression and that the results of Strutt and Van der Ziel (6), Van der Ziel and Versnel (8) and Knol and Versnel (3) can be derived from this assumption. The discussion is independent of any further theoretical calculation of g_0, g_1, i_0, and i_1 (Section 2).

**Their paper is only a preliminary result; a more detailed paper which will give a fuller theoretical discussion seems to be forthcoming.*

It will also be shown that Knol and Versnel's interesting circuit unfortunately gives a power gain less than unity so that a complete noise suppression is of little direct value (Section 3). They show, however, the way in which an improvement in signal-to-noise ratio might be obtained (compare Section 4).

2. Cancellation of all Tube Noise

In order to investigate the problem of a complete noise cancellation consider the grounded cathode circuit of Fig. 2. In order to simplify the calculation of the signal-to-noise ratio the anode circuit in Fig. 2 is short-circuited; it can be easily shown that the signal-to-noise *voltage* ratio at the output of an amplifier is equal to the signal-to-noise *current* ratio in a lead short-circuiting the output. The input admittance Y_g in Fig. 2 consists of a resistance R_a

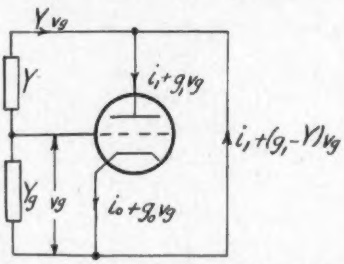

FIG. 2. *Equivalent circuit for the calculation of the noise current due to shot noise in a (grounded cathode) triode amplifier stage with short-circuited output. Owing to the induced grid noise a voltage v_g is developed across the input admittance Y_g, a current $(i_0 + g_0 v_g)$ will flow from the cathode, a current $(i_1 + g_1 v_g)$ will flow to the anode, and a current Yv_g flows through the feedback admittance Y.*

(the transformed antenna resistance) in parallel with a positive or negative capacity C (measuring the detuning of the input circuit). Y is the feedback admittance between input and output. Another simplification is that we neglect noise of the tuned input circuit (this means that the tuned circuit impedance is assumed to be large).

The induced grid noise gives rise to a voltage v_g between grid and cathode; a noise current $(i_0 + g_0v_g)$ flows *from* the cathode, a noise current $(i_1 + g_1v_g)$ flows *to* the anode, a current Yv_g flows through Y and a current $(i_0 - i_1) + (g_0 - g_1 + Y) v_g$ flows through Yg. Hence:

$$(i_0 - i_1) + (g_0 - g_1 + Y) v_g = - Y_g v_g \,; \tag{4}$$

v_g can be determined from this equation. Introducing this expression for v_g into the formula for the noise current i_t in the output lead, we have:

$$\begin{aligned} i_t &= i_1 + (g_1 - Y) v_g = \\ &i_1(Y_g + g_0 - g_1 i_0/i_1 + Y i_0/i_1)\ (g_0 - g_1 + Y + Y_g)^{-1}. \end{aligned} \tag{5}$$

A complete cancellation of all tube noise means that i_t is zero; this leads to the condition:

$$Yg + g_0 - g_1\, i_0/i_1 + Y\, i_0/i_1 = 0. \tag{6}$$

In a similar way it can be shown that for a grounded grid stage with a feed back admittance Y between cathode and anode the condition for zero tube noise becomes:

$$Y + Y_g + g_0 - g_1\, i_0/i_1 - Y\, i_0/i_1 = 0. \tag{7}$$

We first discuss the case of negligible feedback ($Y = 0$). A grounded-grid stage usually has no feedback unless it is introduced purposely, because the anode-cathode capacity can be very small. A grounded-cathode circuit may have an appreciable feedback through the anode-grid capacity C_{ag}; this can be eliminated by tuning this capacity to the center of the desired band. Putting $Y = 0$ in (6) and (7), we obtain in both cases:

$$Y_g + g_0 - g_1\, i_0/i_1 = 0. \tag{8}$$

This is essentially the condition which was first derived by Strutt and Van der Ziel (6).

The question whether a complete noise suppression *without* feedback is possible is determined by the quantity:

$$Y_z = g_0 - g_1\, i_0/i_1 = +j\omega C_z + 1/R_z, \tag{9}$$

which has the dimension of an admittance and which has a real part $1/R_z$. Equation (8) actually means a double condition, one for the real and one for the imaginary part. As Y_g consists of a capacity C in parallel with the resistance R_a we can always satisfy the condition for the imaginary part by a suitable choice of C ($C = -C_z$). However, the condition for the real part is:

$$1/R_a + 1/R_z = 0 \tag{8a}$$

and as R_a is always positive, this can be true only if R_z is negative. Experiments carried out by Van der Ziel and Versnel (8) on grounded grid circuits showed that R_z was positive*. This means that *no* complete noise suppression is possible without feedback.

In order to prove the validity of the results obtained by Knol and Versnel (3) for a grounded cathode circuit with capacitive feedback we turn to (6). Equation (6) also means a double condition; the condition for the imaginary part can again be satisfied by a suitable choice of C; the condition for the real part:

$$1/R_a + 1/R_z + Re\,(Y i_0/i_1) = 0$$

(Re stands for real part) requires further consideration. As R_a and R_z are positive, (6*a*) can be satisfied only if $Re\,(Y i_0/i_1)$ is negative.

i_1 is delayed in phase with respect to i_0, so that we may write:

$$i_0/i_1 = a \exp\,(j\varphi) \tag{10}$$

**The measurements were carried out at 7.25 m. wave length, but as R_z is proportional to ω^2 in a wide frequency range, one would expect R_z to be positive at least in that range.*

For moderately high frequencies $a > 0$ and φ is proportional to ω. Hence we obtain for $Y = j\omega C_1$:

$$Re\ (Y\, i_0/i_1) = -\, a\omega C_1 \sin \varphi, \tag{6b}$$

which is negative because $\varphi < \pi$ for moderately high frequencies. The value of (6*b*) can be made equal to $-\,(1/R_a + 1/R_z)$ by a suitable choice of C_1 for *any* value of R_a. *Hence a complete tube noise suppression can always be obtained by introducing the proper amount of feedback.*

A similar discussion can be given for the grounded grid circuit with a feed-back admittance Y between input and output. The quantity $Y\, i_0/i_1$ occurs in (6) and (7) with different sign; therefore a complete suppression of all tube noise for the grounded grid circuit is possible if a suitably chosen *self-induction* is introduced between cathode and anode.

It has to be borne in mind that a *complete* noise suppression occurs only at one particular frequency, e.g., for the center frequency of the band which has to be amplified. This does not matter so much for narrow band amplifiers, but for wide band amplifiers the improvement in signal-to-noise ratio is greatest near the center of the band and may be much smaller at the edges of the band.

But even if the complete suppression of all tube noise were possible, this does not mean that it would be useful. The circuit would be useful if it had an available power gain > 1; in that case one might connect a number of identical stages (each having zero tube noise) in the right way and so build an amplifier which had zero tube noise but still had a large available power gain. But if the available power gain were < 1, the circuit would be useless as it would decrease the available signal power.

One might think that a separate experiment would be necessary in order to determine which of the two cases actually occurs. But this is not the case; it will be shown in the next section that under the condition of a complete suppression of all tube noise the available power gain g_a becomes:

$$g_a = (1 + R_a/R_z)^{-1}. \tag{11}$$

As R_z was positive we find that $g_a < 1$. Hence we conclude that a *complete suppression of all tube noise in triodes is always possible, but it is not useful to obtain it.*

3. Calculation of the Available Power Gain

We calculate the power gain of the circuit by means of the antenna noise. In Fig. 3 this antenna noise is represented by a current i_a flowing into the input, such that:

$$\overline{i_a^2} = 4kT\Delta\nu/R_a. \tag{12}$$

The antenna noise gives rise to a voltage v_g between cathode and grid and causes a current $g_0 v_g$ to flow *from* the cathode, a current $g_1 v_g$ to flow *to* the anode, and a current Yv_g to flow through Y. According to Fig. 3:

$$i_a = (Y + Y_g + g_0 - g_1)\, v_g, \tag{13}$$

and hence we have for the noise current in the anode lead:

$$i_r = (g_1 - Y)\, v_g = i_a\,(g_1 - Y)\,(Y + Y_g + g_0 - g_1)^{-1}. \tag{14}$$

We know that the available antenna noise power is $kT\Delta\nu$; we also know that the short-circuit current in the anode lead due to antenna noise is i_r; hence if we calculate the internal output impedance of the circuit then we can determine the available output power and the available gain.

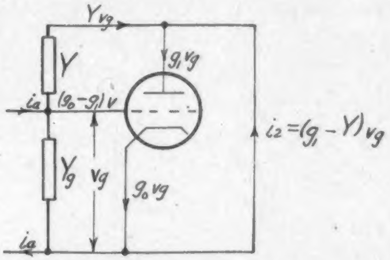

FIG. 3. *Equivalent circuit for the calculation of the noise current in a (grounded cathode) triode amplifier stage with short-circuited output due to antenna noise. The antenna noise gives rise to a voltage v_g across the input circuit; a current g_1v_g flows to the anode and a current g_0v_g flows from the cathode, whereas a current Yv_g flows through the feed-back admittance Y.*

In order to calculate the output admittance of the circuit, consider Fig. 4. The e.m.f. V inserted in the short-circuited anode lead gives rise to a voltage V_g across Y_g, to a current g_0V_g flowing from the cathode, to a current g_1V_g flowing to the anode, and to a current $Y(V - V_g)$ flowing through Y. The current I in the output lead is

$$I = g_1V_g + Y(V - V_g); \tag{15}$$

the current flowing through Y_g is:

$$(g_0 - g_1)\, V_g - Y(V - V_g) = -\, Y_gV_g, \tag{16}$$

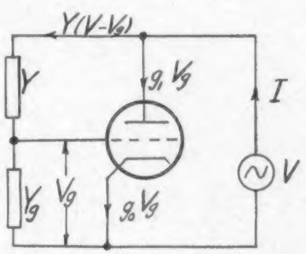

FIG. 4. *Equivalent circuit for the calculation of the output admittance Y_0 of a (grounded cathode) triode amplifier stage containing a feed-back admittance Y between input and output. In order to calculate Y_0, a voltage V is applied to the short-circuited output, the current I flowing into the circuit is calculated and Y_0 is defined as I/V. The voltage V gives rise to a voltage V_g across the input, to a current g_0V_g flowing from the cathode, and to a current g_1V_g flowing to the anode, whereas a current $Y\,(V - V_g)$ is flowing through the feed-back admittance Y.*

which can be solved for V_g:

$$V_g = Y\,V\,(Y + Y_g + g_0 - g_1)^{-1}. \tag{17}$$

Introducing this into (15) and putting I/V equal to the output admittance Y_0 of the circuit, we obtain:

$$Y_0 = I/V = Y\,(Y_g + g_0)\,(Y_g + Y + g_0 - g_1)^{-1}. \tag{18}$$

Therefore the output of the stage is equivalent to an output e.m.f.:

$$e_r = i_r/Y_0 = i_a\,(g_1 - Y)\,Y^{-1}\,(Y_g + g_0)^{-1} \tag{19}$$

in series with an output impedance:

$$Z_0 = R_0 + jX_0 = Y_0^{-1} = Y^{-1}\,[1 - (g_1 - Y)\,(Y_g + g_0)^{-1}], \tag{20}$$

where R_0 is the real part of Z_0. The available power P_0 is then $\frac{1}{4}\overline{e_r^2}/R_0$, and, as the available input power P_a was $kT\Delta\nu$, we find for the available power gain g_a:

$$g_a = P_0/P_a = \overline{e_r^2}\,(4kTR_0\Delta\nu)^{-1} = R_a^{-1}\left|(g_1 - Y)\,Y^{-1}\,(Y_g + g_0)^{-1}\right|^2. \tag{21}$$

We now introduce the condition for a complete noise cancellation:

$$(Y_g + g_0) - (g_1 - Y)\,i_0/i_1 = 0 \tag{6}$$

and write it in two ways; first as:

$$(g_1 - Y)\,(Y_g + g_0)^{-1} = i_1/i_0 \tag{22}$$

and then for the real part of (6):

$$1/R_a + 1/R_z + Re\,(Yi_0/i_1) = 0, \tag{6a}$$

where Re again means "real part of". Introducing (22) into (20) we obtain:

$$Z_0 = R_0 + jX_0 = Y^{-1} - (Y\,i_0/i_1)^{-1}. \tag{23}$$

As Y is completely imaginary, we have under the condition of complete noise suppression:

$$\begin{aligned} R_0 &= -\,Re\,(Y\,i_0/i_1)^{-1} = -\left|Y\,i_0/i_1\right|^{-2} Re(Y\,i_0/i_1) = \\ &= (1/R_a + 1/R_z)\left|Y\,i_0/i_1\right|^{-2} \end{aligned} \tag{24}$$

by (6a). Introducing (22) into (21) we obtain:

$$g_a = R_a^{-1}R_0^{-1}\left|Yi_0/i_1\right|^{-2} = (1 + R_a/R_z)^{-1} \tag{25}$$

by (24). This is exactly Formula (11) which was to be proved.

4. Calculation of the Noise Factor

We saw that a complete suppression of all tube noise, though perfectly possible in the case of complete correlation, was not useful. But it should still be possible in that case to improve the signal-to-noise ratio quite considerably in many cases by adopting a different method of attack. One

calculates the available gain g_a of the circuit and the noise factor F. One then keeps g_a at a fixed value > 1 (e.g., $g_a = 3$); this gives one condition for the circuit parameters. One then introduces this condition into the expression for F and determines the transformed antenna resistance R_a, the detuning of the input circuit (capacity C) and the feed-back capacity C_0 such that F attains a minimum value for the above fixed value of g_a.

As the available power was calculated in Section 3, we only have to calculate the noise factor F. The noise factor is the ratio of the actual output noise power to the output power which would have been present if the antenna were the only noise source and if its noise temperature were equal to the normal room temperature T. According to (5) the tube noise gives a mean square noise current $\overline{i_t^2}$ and from (14) the antenna noise gives a mean square noise current $\overline{i_r^2}$; hence the noise factor F is:

$$F = 1 + \overline{i_t^2}/\overline{i_r^2} = 1 + R_n R_a |g_1 (g_1 - Y)^{-1}|^2 \cdot |Y_g + g_0 - g_1 i_0/i_1 + Y i_0/i_1|^2, \tag{26}$$

in which R_n (the equivalent noise resistance) is introduced by the relation:

$$\overline{i_1^2} = 4kTR_n\Delta\nu|g_1|^2,$$

whereas $\overline{i_a^2}$ (which occurs in $\overline{i_r^2}$) follows from (12).

The wavelength region where such a noise reducing circuit might be useful depends upon the magnitude of the induced grid noise. Above 10 m. the induced grid noise is not very large and the noise of the tuned circuit becomes the predominant factor. At shorter wave lengths (1 to 10 m.) the situation is more favorable, because the induced grid noise becomes much more important ($\overline{i^2}$ and $1/R_{el}$ increase as ω^2). At very high frequencies (below 1 m. wave length) the improvement in noise factor at a suitable power gain depends strongly upon the phase angles of i_0, i_1, g_0, and g_1, so that experiments must be made to decide how much improvement can be obtained.

5. Conclusions

Whether or not such a minimum noise circuit will be used in practice depends upon the requirements which have to be met, and upon the improvement which can be obtained. This depends largely upon the following factors:

1. In theoretical discussions it is assumed that i_0 and i_1 are completely correlated. Measurements must be made to decide whether this is true.

2. The theory does not incorporate the contribution of the thermal noise of the input circuit to the noise factor. Theoretically this contribution can be made quite small but in practice (owing to limitations in space and costs) there is a definite upper limit of the circuit impedance and this will determine the lower limit of the noise factor which can be obtained.

3. The circuit is a feed-back circuit and therefore, though it may be perfectly stable at the signal frequency, it might have the tendency to oscillate at a slightly different frequency.

Measurements are now in progress in order to obtain answers to these problems and to determine how much improvement in noise factor is feasible in practice. We hope to publish the results in the near future.

Acknowledgment

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THE ARSENIC, LEAD, TIN, COPPER, AND IRON CONTENT OF CANNED CLAMS, OYSTERS, CRABS, LOBSTERS, AND SHRIMPS[1]

JAMES DICK[2] AND L. I. PUGSLEY[3]

Abstract

A survey of the heavy metal content of canned shellfish and crustaceans sold on the Canadian market has been made. With the exception of one sample of clams having 5 p.p.m. of lead, one sample of lobster having 13 p.p.m. of lead and, one sample of lobster having 7 p.p.m. of arsenic, of the 120 samples analyzed the values found were not significantly above the limits established for the heavy metal content of foods.

Introduction

Chapman and Linden (1) reported values for the heavy metal content of shell fish and crustaceans collected in the Thames estuary, England, which exceeded considerably the limits established for foods under the Regulations of the Food and Drugs Act of Canada. Although no systematic survey of these products for heavy metals has been made, values of the magnitude reported by Chapman and Linden (1) had not been encountered in the regulatory work of the Food and Drug Divisions. Additional information on the metallic content of these foods has not been encountered, and a survey of these products as sold on the Canadian market appeared of interest.

Methods

Samples consisting of six cans each were taken at random from the different brands of stocks of canned crabs, lobsters, shrimps, clams, and oysters available in retail stores at Vancouver, Ottawa, and Halifax. The number of brands, species, and place of packing of each of the canned shellfish or crustaceans analyzed are shown in Table I.

The contents of each can was thoroughly mixed by placing it in a Waring blendor for five minutes, using a measured amount of water in the case of solid meats to obtain the necessary constituency for mixing. The total solids were determined by drying an aliquot of the mixed sample in an air-circulated oven at 100° C. to constant weight. Arsenic was determined by the Gutzeit method as outlined in Reference (3). Lead, copper, tin, and iron were determined spectrographically using a Hilger E 1 spectrograph and step sector. Aliquots of each of the mixed samples were digested with nitric acid, the excess nitric acid removed by evaporation, and the residue placed in a muffle furnace at 400° C. for approximately four hours. The

[1] *Manuscript received February 14, 1950.*
Contribution from Food and Drugs Laboratory, Department of National Health and Welfare, Ottawa, Canada.
[2] *Chemist.*
[3] *Chief, Laboratory Services.*

TABLE I

THE NUMBER OF BRANDS, SPECIES, AND PLACE OF PACKING OF THE SAMPLES OF SHELLFISH AND CRUSTACEANS

Brand	Name	Place of packing
1, 2	Crab meat (*Cancer magister*)	Masset, B.C.
3, 4	" " " "	Vancouver, B.C.
1, 2	Lobster (*Homarus americanus*)	Charlottetown, P.E.I.
3	" " "	Saint John, N.B.
1, 2	Shrimp (*Peneus setiferous*)	New Orleans, La.
3, 4	" " "	Biloxe, Miss.
5	" " "	Bayow La Batre, Ala.
1	Clams (*Mya arenaris*)	Five Islands, N.S.
2	" " "	Padagon, N.B.
3	" " "	Charlottetown, P.E.I.
4	" (*Saxidomus giganteus*)	Vancouver, B.C.
1	Oysters (*Ostrea virgenia*)	New Orleans, La.
2	" (*Ostrea gigas*)	Vancouver, B.C.
3	Smoked oysters (*Ostrea gigas*)	Vancouver, B.C.

ignited residue was made up to volume with acidic (hydrochloric acid) 20% sodium chloride to which bismuth chloride was added as an internal standard. An aliquot equivalent to 35 mgm. of the residue was evaporated to dryness and the metals determined spectrographically. The relative intensity of the bismuth to the selected line of the metal in question was determined with a Hilger recording photo-electric microphotometer. The principles of the spectrographic method used is utlined by Cholak and Story (2). The results are shown in Table II, where the total solids are expressed in per cent; arsenic as As_2O_3, lead as Pb, tin as Sn, copper as Cu, and iron as Fe, as parts per million, wet weight. Since there was no significant difference between brands, except in the case of oysters and smoked oysters, the mean

TABLE II

TOTAL SOLIDS, ARSENIC, LEAD, TIN, COPPER AND IRON CONTENT OF CANNED SHELLFISH AND CRUSTACEANS

Product	No. of samples	Total solids, %	Arsenic trioxide, p.p.m.	Lead, p.p.m.	Tin, p.p.m.	Copper, p.p.m.	Iron, p.p.m.
Clams	24 4 brands	15.9 ± 1.30 14.1 – 17.7	0.48 ± 0.77 0.0 – 3.5	0.81 ± 1.09 0.0 – 5.0	3.20 ± 2.87 0.0 – 12.0	2.46 ± 1.77 0.0 – 7.0	64.1 ± 32.5 7.0 – 110.0
Oysters	12 2 brands	16.0 ± 1.62 14.0 – 20.2	0.29 ± 0.50 0.0 – 1.5	0.83 ± 0.96 0.0 – 2.5	0.92 ± 0.51 0.0 – 2.0	37.7 ± 17.4 15.0 – 65.0	47.8 ± 16.2 19.0 – 80.0
Oysters Smoked	6 1 brand	45.8 ± 1.37 44.4 – 47.6	1.33 ± 1.17 0.0 – 3.0	0.33 ± 0.52 0.0 – 1.0	28.33 ± 2.58 25.0 – 30.0	16.0 ± 4.47 12.0 – 23.0	37.3 ± 7.94 25.0 – 45.0
Crabs	24 4 brands	25.0 ± 0.73 23.7 – 26.8	0.94 ± 1.40 0.0 – 4.0	0.17 ± 0.24 0.0 – 0.50	3.58 ± 1.67 0.0 – 6.0	3.25 ± 1.51 1.0 – 7.0	7.21 ± 7.74 0.0 – 30.0
Lobsters	18 3 brands	22.1 ± 1.47 20.1 – 24.6	1.25 ± 1.91 0.0 – 7.0	1.03 ± 3.01 0.0 – 13.0	4.11 ± 1.91 1.0 – 8.0	12.67 ± 5.32 6.0 – 25.0	8.11 ± 5.77 1.0 – 25.0
Shrimps	30 6 brands	19.9 ± 1.23 18.3 – 23.6	0.10 ± 0.24 0.0 – 1.0	0.48 ± 0.50 0.0 – 1.5	1.83 ± 1.26 0.0 – 5.0	2.77 ± 2.10 0.0 – 11.0	15.5 ± 12.5 3.0 – 60.0

of the samples is shown with ± 1 standard deviation and the range of the values encountered in the samples analyzed immediately below the mean value.

Discussion

It is noted that the arsenic and lead values are relatively low in all products except in the case of lobster where one sample showed 13 p.p.m. with respect to lead and one sample showed 7.0 p.p.m. with respect to arsenic.

In regard to the other constituents, the low values of tin present point to the efficiency of the enamel lining in protecting the tin plated cans from corrosion. The low amount of tin present also indicates that the products derive their metallic content from the shellfish themselves and not from extraneous sources. In the case of smoked oysters where the tin content was between 25 and 30 p.p.m. it would appear that this metal is derived from plant equipment in the smoking process rather than from the oysters themselves, especially as zinc which was practically absent in other samples of oysters was observed to be distinctly present in the smoked oysters. In accordance with the experience of this Laboratory clams have a relatively high iron content. In these samples the iron content of the clams from the East coast were relatively higher than those from the West coast. In comparison with the other shellfish and crustaceans analyzed, oysters show a relatively higher content of copper.

The results of this survey indicate no serious contamination of canned shellfish and crustaceans with toxic metals, in contrast to the values reported by Chapman and Linden (1). The high values encountered with shellfish from the Thames estuary may be due to the accumulation of extraneous material in the shellfish beds of this heavy shipping lane. On this continent, freedom from heavy shipping lanes in the vicinity of the shellfish beds may be a factor in the lower heavy metal content of the products.

Acknowledgment

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EXTRACTION, FRACTIONATION, AND EVALUATION OF CARRAGEENIN[1]

By R. C. Rose[2]

Abstract

The amount of carrageenin extracted from a sample of rinsed *Chondrus crispus* increased linearly with temperature of extraction up to 100° C., and more slowly thereafter up to 110° C. Increasing the temperature to 125° C. had no further effect on the yield. Heat treating carrageen or replacing the calcium and potassium in it with sodium increased the yield of carrageenin at lower temperatures.

The viscosity of carrageenin extracts obtained at different temperatures increased and the concentration required to increase the viscosity of milk to 15 centistokes (i.e., the "suspending concentration" for cocoa in milk) decreased with temperature of extraction up to 60° C. Above this temperature the viscosity decreased and the suspending concentration increased. The increase in viscosity is attributed to the extraction of higher polymers of carrageenin with increased temperature; the decrease, to heat depolymerization during extraction. Neither the solubility nor the fractionation studies gave any indication of chemically distinct carrageenin components. The essential difference between carrageenin that was most effective if incorporated with cold milk and carrageenin that was most effective if incorporated with hot milk was that the former was of high suspending concentration. A method of evaluating carrageen which gives soluble carrageenin divided by suspending concentration was tested but the results were sensitive to variations among samples of milk. When the same milk was used, the correlation coefficient between the concentration required to give viscosities of 15 centistokes in milk and in 0.05 *N* sodium chloride for 12 samples was .93. Viscosity in 0.05 *N* sodium chloride is preferred for evaluation of carrageen.

Introduction

The value of carrageen (*Chondrus crispus*) depends upon the yield and quality of carrageenin which can be extracted from it; both yield and quality are effected by the conditions of extraction. Three carrageen extracts have been distinguished in the literature on the basis of the temperature of extraction: 40–50°C., called a cold extract; 80–100°C., called a hot extract; and 115–120°C., called a pressure extract. Once extracted, all of these products are water soluble at 50°C. The cold extract and the pressure extract are reported to be nongelling (3, 5) whereas a 1 to 2% solution of the hot extract normally gels readily. The hot extract and the pressure extract are used to stabilize chocolate milk but the hot extract is most effective if incorporated in hot milk whereas commercial pressure extract can be as effectively mixed with cold as with hot milk if first dissolved as a more concentrated solution in water (5). No information appears to be available on the stabilizing power of the cold extract. The cold extract is principally the sodium and potassium salt of carrageenin and the hot extract is chiefly the calcium salt (1). The cation can be exchanged (2). Hot extracts lose their gelling properties when the

[1] *Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as Paper No. 3 of the Associate Committee on Seaweed Research and as N.R.C. No. 2148.*

[2] *Biochemist.*

calcium in them is replaced with sodium. Differences in cation among the extracts do not appear to account for their differences in reactivity with milk.

Obviously the conditions of extraction affect the proportion of these products which can be obtained from any one sample of carrageen. A commercial practice is to rinse the dried weed in cold water to remove salts, extract at 80–85°C. (commercial "hot extract") and then extract under pressure. Commercial hot extracts therefore contain the "cold extract" as well.

In the present work, factors affecting extraction and the properties of fractions, particularly their chocolate milk stabilizing properties, were studied and compared with those of commercial carrageenin. An empirical method of extracting carrageenin was adopted and used, in conjunction with measurements of properties, to evaluate different samples of carrageen.

Materials and Methods

Samples of carrageen were obtained from Nova Scotia, Prince Edward Island, Maine, and France. All samples had been dried and some were sun bleached. They were ground in a Wiley mill to pass a 2 mm. screen. Weighed portions were rinsed for 10 min. by stirring in about 40 times their weight of tap water at 20°C., strained, and then extracted at the desired temperature with stirring. A household pressure cooker and a magnetic stirrer were used for temperatures above 100°C. At the end of extraction the mixture was weighed and centrifuged; the solution was strained through a course fritted glass filter funnel and weighed. Some of the extract was filtered and the concentration determined by drying a portion in vacuum at 80°C. overnight and weighing; carrageenin was also estimated by precipitation with benzidine (4). Portions were diluted to 0.20% dry matter, made 0.05 N with respect to

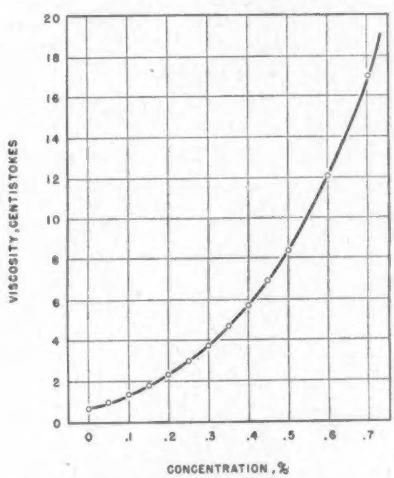

FIG. 1. *Viscosity of carrageenin at 40° C. in 0.05 N sodium chloride.*

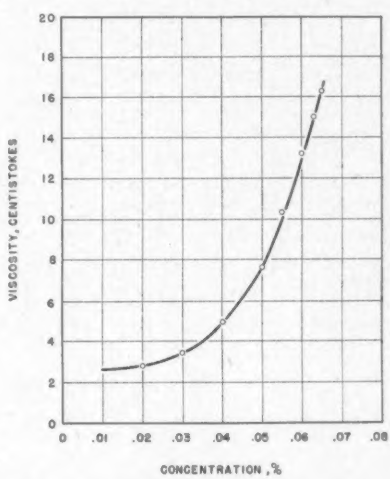

FIG. 2. *Viscosity of carrageenin at 10° C. in milk.*

sodium chloride, and their viscosities were measured at 40°C. Portions were also diluted as required and added to milk in the ratio of 10 ml. of carrageenin solution of 90 ml. of milk. They were then refrigerated overnight and viscosities (first flow times) at 10°C. determined as previously described (6) with Fenske modified Ostwald Viscometers. Commercial samples of carrageenin were used for comparison.

The relation between viscosity at 40°C. and concentration of carrageenin in 0.05 *N* sodium chloride, and the relation between viscosity at 10°C. and concentration of carrageenin in milk with 10% added water, were determined for one sample. The resulting curves, Fig. 1 and 2, were used as references, in conjunction with viscosity measurements on other samples, to estimate the relative concentration factors of the samples in 0.05 *N* sodium chloride and in milk, respectively (6).

Previous work (6) had shown that the concentration of carrageenin needed to increase the viscosity of milk to 15 centistokes at 10°C. was a reliable measure of suspending concentration for 2% cocoa in milk. Consequently, in the present work, viscosity of cocoa-free milk was used exclusively to estimate suspending concentration.

Experimental

Effect of Temperature on the Extraction of Carrageenin

Preliminary tests, in which 10-gm. samples of carrageenin were extracted for 0.5, 1, and 2 hr. at 100°C. and made to the same weight of mixture, gave concentrations of 0.258, 0.266, and 0.271%. A time of one hour was adopted in the main series, for convenience. Each sample was extracted after rinsing, for three one-hour periods, using about 100 gm. of water per gram of original weed, then weighed, filtered, and the filtrate weighed and its concentration determined. The amount extracted was calculated from the concentration and weight of each filtrate. To calculate the total amount of soluble carrageenin at the end of first extraction, the concentration of the filtrate was multiplied by the weight of slurry, i.e., the weight of carrageenin solution prior to filtering; the assumption is thus made that the concentration of soluble carrageenin in the swollen weed residue is the same as in the filtrate. The values for the total amount of soluble carrageenin are independent of the proportion of solution obtained in the filtrate. The results, Table I, show an approximately linear relation between temperature and extraction up to 100°C. and a levelling off above this temperature. At 110°C. and higher the soluble carrageenin after first extraction equalled the total extraction. Below 110°C., total extraction exceeded soluble carrageenin after first extraction, which suggests that prolonged heating converted more carrageenin to the soluble form.

The composition of the carrageen used in this study was: moisture 14.7%, loss on rinsing 12.5%, carrageenin (mean of last four values in Table I) 54.8%, sand 10.2%, organic residue 7.8%, all by weight.

TABLE I

EFFECT OF TEMPERATURE ON THE EXTRACTION OF CARRAGEENIN
(Values expressed as weight % of weed used)

Temperature, °C.	Soluble carrageenin after first extraction, %	Extraction, %			
		1st	2nd	3rd	Total
20	3.1	2.9	2.0	1.1	6.0
40	10.9	9.3	3.6	3.9	16.8
60	24.1	20.9	5.9	1.8	28.6
80	34.6	27.6	6.4	2.6	36.6
100	46.7	38.6	8.4	5.3	50.3
	47.4	37.7	11.3	1.8	50.8
110	54.6	45.2	7.2	2.2	54.6
	54.0	46.8	6.1	1.0	53.9
120	56.0	48.1	6.5	1.4	56.0
125	54.7	—	—	—	—

Effect of Cation, Salt, and Heat Treatment on Extraction of Carrageenin

Cations affect gelling, and therefore solubility of carrageenin. As sodium and potassium predominate in the cold extract and calcium is the principal cation in the hot extract, the possibility existed that replacing calcium in the weed with sodium would make all of the carrageenin soluble at a lower temperature. Weighed amounts of carrageen were dialyzed with stirring against solutions (which were changed several times) of sodium chloride, potassium chloride, and calcium chloride, respectively. They were then dialyzed at 5°C. against distilled water to remove excess salt, and finally extracted for three one-hour periods. Samples of 10 gm. of carrageen were also extracted in the presence of 4 gm. of sodium oxalate and a trace of sodium carbonate to increase the pH.

The amounts extracted at 40°C. were: after dialyzing against sodium chloride or adding sodium oxalate, 32%; after dialyzing against potasium chloride, 10.7%; and after dialyzing against calcium chloride,, 8.3%; compared with 16.8% with rinsed carrageen. At 60°C. the amount extracted was almost independent of the cation present.

Some carrageen was extracted at 100°C. in 0.2% sodium chloride solution. This salt concentration had no measurable effect on the extraction of carrageenin but it appeared to reduce the swelling of the seaweed and it increased the proportion of the filtrate obtained. In addition, the solutions containing salt filtered much more readily—probably owing to their lower viscosity (18 centistokes at 40°C. compared with 50 centistokes in the absence of salt).

A brief series of tests were run to determine if heat treating carrageen would increase the amount of carrageenin extracted at lower temperatures. Rinsed samples of carrageen were brought to moisture levels of 0, 20, and 50% (vacuum drying over phosphorus pentoxide at room temperature was used to obtain the dry sample), and heated in sealed containers for one hour

at 100°C. After heating, the samples were extracted for three one-hour periods at selected temperatures. The results showed that the amounts extracted at 40°C. and at 60°C. were independent of the moisture level during heat treatment. At both 40°C. and 60°C. the amount extracted averaged 36% compared with yields of 16.8% and 28.6% at these temperatures when non-heat-treated weed was used. As previous results had shown that extraction was independent of cation above 60°C., a combination of heat treatment and cation exchange was not investigated.

Although the yield at 40° C. was increased by heat treatment and by dialysis against sodium chloride it did not equal that obtained at 100° C. with non-heat-treated weed.

Properties of Carrageenin Fractions

Carrageenin fractions were obtained by extracting carrageen at specific temperature spreads; each extraction was for 30 min. and the amount of water used was chosen, from results in Table I, to give a carrageenin concentration of 0.3 to 0.5%. One sample was extracted at 30, 40, 60, 80, and 100° C.; to obtain the 110° C. fraction a second sample was extracted at 100° C. (extract discarded) and then extracted at 110° C. Concentration was determined by drying, by precipitation in 70% alcohol containing 0.2% calcium chloride, and by precipitation with benzidine (4). Viscosities of 0.2% (dry basis) solutions in 0.05 *N* sodium chloride and suspending concentrations were determined. As the fractions obtained had received increasingly severe heating during extraction, portions of the extracts (with the exception of that obtained at 110° C.) were heated for one hour at 100° C. and the viscosities and suspending concentrations redetermined.

The results are given in Table II. They show that viscosity increased and suspending concentration decreased as the extraction temperature increased up to 60° C.; above 60° C. viscosity decreased and suspending concentration

TABLE II

PROPERTIES OF CARRAGEENIN FRACTIONS

Fractionation temp., ° C.	Viscosity in 0.05 *N* sodium chloride, centistokes		Precipitation by alcohol, % of dry matter	Precipitation by benzidine, % of dry matter	15 centistoke concentration in milk, %			
					On dry basis		On benzidine precipitation basis	
	Original	After heating			Original	After heating	Original	After heating
20-30	2.2	1.2	70	57	0.070	0.083	0.040	0.047
30-40	5.9	1.9	90	95	0.034	0.040	0.032	0.038
40-60	13.4	5.1	95	100	0.020	0.026	0.020	0.026
60-80	9.4	4.2	90	100	0.023	0.026	0.023	0.026
80-100	8.5	4.9	90	102	0.025	0.027	0.026	0.028
100-110	3.2	—	—	105	0.033	—	0.035	—

increased. Benzidine, which acts on the sulphate group of carrageenin, precipitated only 57% of the first fraction and 95% of the second. This suggests that these fractions contained noncarrageenin components.

Effect of Adding Carrageenin to Hot and to Cold Milk

Commercial pressure extracts of carrageen can be mixed with cold milk to suspend cocoa whereas hot extracts should, according to a patent (5), be mixed with hot milk. To examine possible differences among samples of carrageenin, viscosity concentration curves for several commercial hot extracts and pressure extracts were determined. The method of preparing the solutions was to weigh out the desired amount of carrageenin, dissolve it in 10 ml. of hot water, cool to 30–40° C. (lower temperatures were apt to cause gelling) and then add 90 ml. of milk which was either at 10° C. or 60° C. and mix vigorously. Hot milk solutions were then cooled under the tap and all solutions were refrigerated overnight prior to measuring their viscosity at 10° C.

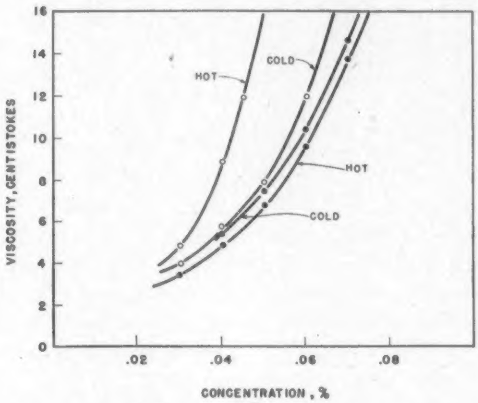

FIG. 3. *Effect of adding commercial high quality carrageenin and commercial pressure extracted carrageenin to hot and to cold milk on the viscosity.*
○ *Commercial high quality carrageenin*
● *Commercial pressure extracted carrageenin*

Typical results are shown in Fig. 3. A commercial good quality (low suspending concentration) hot extract had a suspending concentration (15 centistoke) when incorporated with hot milk of 0.049% but this concentration only gave a viscosity of 7.6 centistokes when incorporated with cold milk. The suspending concentration with cold milk was 0.065%. A commercial pressure extract, on the other hand, had a high suspending concentration and was more effective when mixed with cold milk than when mixed with hot milk.

This suggested that high suspending concentration was the essential property of extracts which were as good with cold milk as with hot milk. To examine this possibility the hot extract of highest suspending concen-

tration on hand was tested. The hot extract, the results for which are given in Fig. 3, was also subjected to very mild acid hydrolysis, neutralized, and re-examined. The results (Fig. 4) show that both samples were more effective when mixed with cold milk than when mixed with hot milk. This

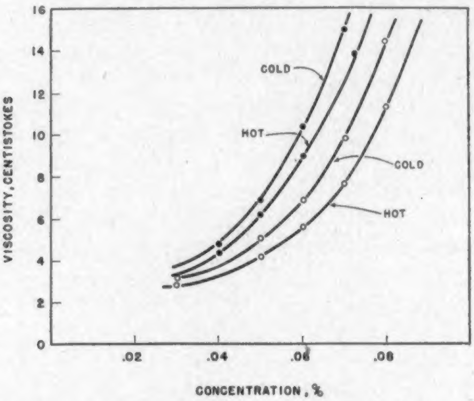

FIG. 4. *Effect of adding low quality carrageenin to hot and to cold milk on the viscosity.*
• *Commercial low quality carrageenin*
○ *Hydrolysed commercial high quality carrageenin*

confirms the relation between high suspending concentration and relative effectiveness when the carrageenin is mixed with cold milk. The results show, however, that even with cold milk the good quality hot extract, although not so good as with hot milk, was more effective in these laboratory tests than any of the other samples. This, however, might not apply on an industrial scale where mixing conditions are different.

Evaluation of Carrageen

The results already given show that the yield of carrageenin increased with increasing temperature up to 110° C. and that suspending concentration increased with increasing temperatures above 60° C. From the standpoint of chocolate milk stabilization the value of a sample of carrageen is proportional to the yield divided by the suspending concentration. To determine the best extraction conditions, carrageen samples were rinsed and then heated with 1500 ml. of water per 10 gm. of weed. At the end of heating the carrageen slurry was weighed, centrifuged, and the extract filtered. Sodium chloride was added to a portion of the filtrate to make it 0.05 *N* and the viscosity determined at 40° C. By reference to Fig. 1 the dilution required to reduce the viscosity to 5 to 8 centistokes was estimated and a portion of the original extract was so diluted. This dilution was necessary, as too much carrageenin curdles milk. Then 10 gm. of this diluted extract was added to 90 gm. of milk at 60° C. and, after refrigeration, the viscosity

was determined at 10° C. By reference to Fig. 2 the volume of diluted extract needed to increase the viscosity of milk to 15 centistokes was estimated. Then $M = \dfrac{100Wd}{10w}$, where

M = weight of milk of which the viscosity can be increased to 15 centistokes by the extract from 1 gm. of carrageen, gm.
W = weight of carrageen slurry from 10 gm. of carrageen, gm.
d = dilution required to reduce viscosity in 0.05 N sodium chloride to 5 to 8 centistokes, i.e., the ratio of the weights of diluted to undiluted carrageenin solution.
w = weight of diluted extract needed to increase the viscosity of milk to 15 centistokes, gm.
(The factor 100 comprises 90 of milk and 10 of extract. The 10 is introduced in the denominator as 10 gm. of carrageen were used.)

Similarly the weight of 0.05 N sodium chloride of which the viscosity can be increased to a specified level (e.g., 15 centistokes) by the extract from 1 gm. can be determined. As the total weight of carrageen slurry was used in the above equation the results are independent of the proportion of filtrate and sludge.

The M values obtained in a series of tests on time and temperature of extraction are shown in Table III. Extraction in dilute sodium carbonate solution gave higher results than when water was used. The longer heating time had little effect. Analyses showed that this was due to the yield and 15 centistokes concentration increasing proportionately during the longer extraction.

In the next series, 12 different samples of *Chondrus crispus* were extracted. The samples were rinsed—although with Sample 2 this was shown to remove

TABLE III
M VALUES OF 15 CENTISTOKE 0.05 N
SODIUM CHLORIDE AND MILK

Extraction time, hr.	M values in 0.05 N sodium chloride			M values in milk		
	Extraction temp., ° C.			Extraction temp., ° C.		
	80	100	110	80	100	110
In water						
0.5	152	166	122	1260	1870	1240
1.0	152	172	120	1300	1900	1250
In 0.1% sodium carbonate						
0.5	152	194	196	1390	2130	2060
1.0	148	202	214	1320	2140	2090

a small amount of carrageenin. Boiling water (containing sodium carbonate) was added to the rinsed carrageen in a large beaker which was then placed in a bath of boiling water and the bath covered. The mixture was thus surrounded with live steam. It was stirred by means of a stirrer which projected through the bath cover. A heating time of 45 min., from the time of adding boiling water, was adopted. The concentration of the extract was determined by evaporating a portion and correcting for the sodium carbonate present. The results for duplicate extractions are shown in Table IV. The solutions of carrageenin in milk were all prepared on the same day with the same milk.

Some of the carrageen extracts were tested with a second lot of milk and the M values averaged 380 gm. higher than those given in Table IV—a difference which is largely attributed to differences in the milk.

TABLE IV

EVALUATION OF CARRAGEEN SAMPLES AND OF CARRAGEENIN EXTRACTS

Sample	Origin	Appearance	M value, gm. of 0.05 N sodium chloride	M value, gm. of milk	Soluble carrageenin, % of original carrageen	15 centistoke concentration in milk, %
1	France	Bleached	38 44	660 700	39.4	0.060
2	P.E.I.	"	61 62	1000 990	37.5	0.038
3	N.S.	"	110 113	1570 1540	52.9	0.034
4	N.S.	Black	135 128	1630 1530	55.4	0.034
5	N.S.	Bleached	140 129	1990 1800	52.8	0.027
6	Maine	Black	140 138	2100 2020	54.0	0.026
7	P.E.I.	Bleached	148 148	1860 1860	49.5	0.027
8	P.E.I.	"	158 153	2020 2100	55.4	0.027
9	P.E.I.	Black	159 159	2080 2040	60.5	0.029
10	P.E.I.	"	159 166	1740 1760	54.0	0.031
11	Maine	"	172 174	2020 1980	55.0	0.027
12	N.S.	Bleached	225 218	2320 2210	56.7	0.024

Statistical analyses of the values in Table IV showed that the variance of duplicate measurements gave a standard deviation of $\pm$ 57 gm. in the weight of milk which can be increased to 15 centistokes. This is about 3.3% of the mean value of 1703 gm. However, as reported above, changing to another sample of milk gave a variation of 380 gm.

With aqueous salt solutions the standard deviation was $\pm$ 3.7 gm., about 2.7% of the mean value of 136.5 gm. The coefficient of linear correlation between the weight of aqueous salt solution and the weight of milk which can be raised to 15 centistokes by the extract from 1 gm. was .93. The corresponding regression equation was:

$$M_m = 494 + 9.065\ M_s,$$

with a standard error of estimate from duplicate determinations of $\pm$ 182,

where M_m = value for milk, and

M_s = value for 0.05 N sodium chloride (mean of duplicates), gm.

A quadratic equation fitted the data significantly better and the multiple correlation coefficient was then .96.

Summary and Discussion

Neither the extraction study of carrageen nor the fractionation study gave any indication of chemically distinct carrageenin components. The latter study showed that as the temperature of extraction increased, up to 60° C., the viscosity of the resulting extract increased and the suspending concentration decreased; above 60° C. viscosity decreased and suspending concentration increased with increasing temperature of extraction. If viscosity is accepted as a measure of molecular complexity, the results indicate that up to 60° C. higher temperatures extracted higher polymers of carrageenin; above 60° C., heat depolymerization during extraction was apparent. The effect of heat treatment on the viscosity of extracts supported the view that depolymerization occurred during extraction at the higher temperatures.

The method of obtaining M values may be of use commercially in evaluating samples of carrageen. The viscosity of milk containing carrageenin was previously shown to be a reliable measure of suspending power (6) and the present work has shown that the method of extraction and testing gives consistent results with the same milk. However, different lots of milk gave wide variations and this, coupled with the high correlation coefficient between 15 centistoke concentration in milk and in 0.05 N sodium chloride (.93 in this study and .90 previously), suggests that viscosity of aqueous solutions may be the more useful measure of suspending concentration.

Acknowledgments

Appreciation is expressed to Mr. J. L. Labelle for technical assistance, to the Algin Corporation of America, Kraft Food Company, Krim-Ko Corporation, and Myrick McIntosh Ltd. for samples of carrageen and carrageenin.

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THE SUSPENDING POWER OF DETERGENT SOLUTIONS

I. PURE SOAPS[1]

A. S. WEATHERBURN[2], G. R. F. ROSE[2] AND C. H. BAYLEY[2]

Abstract

The ability of soaps to prevent the deposition of carbon black and other materials on fabric during the detergent process has been investigated. In general the suspending power of the soap solutions studied increased rapidly with increasing soap concentration, and reached a maximum at a relatively low concentration. At higher concentrations the suspending power either remained constant or decreased slightly. With carbonaceous soils the indicated suspending power for a given soap increased, in general, with increasing particle size and decreasing "structure" of the carbon. With various soiling materials differences were encountered, not only in the magnitude of the indicated suspending power, but also in the form of the curve obtained on plotting suspending power vs. soap concentration. As measured by one type of carbon black (Standard Micronex) only minor differences were found between suspending powers of sodium myristate, palmitate, and stearate, all of which were higher than that of the laurate. Increasing temperatures caused a decrease in the suspending power of the lower chain length soaps (C_{12}, C_{14}) and an increase in the suspending power of the longer chain soaps (C_{16}, C_{18}). The suspending power of sodium oleate was essentially unchanged by temperature variations over the range 25–80°C.

The removal of soil from textile fibers by means of aqueous detergent solutions is a process of considerable complexity. While it is highly probable that other factors contribute to this process, it has been pointed out by Hill (11) and others that a satisfactory detergent solution must be effective with respect to at least three properties, viz.: (*a*) the ability to wet out the surfaces of the fibers and soil and to displace entrapped air from between the fibers ("wetting power"); (*b*) the ability to overcome the adhesional forces which bind the soil to the fiber, and to emulsify oily constituents which may be present, thus facilitating the removal of soil by mechanical action ("soil removing power"); (*c*) the ability to hold the particles of released soil in suspension and thus prevent their redeposition on the fabric ("suspending power").

Numerous methods have been proposed for the measurement of detergency in laundering. In most of these methods standardly soiled fabrics are subjected to the action of detergent solutions under specified conditions. The extent of the detergent action is measured by the increase in whiteness of the fabric (4, 16, 20, 22, 23, 25), by the decrease in weight of the fabric (21), or by the decrease in light transmission of the liquor due to suspended soil particles (29). Such methods provide an empirical means of evaluating detergent compounds although the complexity and unsatisfactory reproducibility of behavior of many of the so-called "standard soils" that have been used casts considerable doubt on the advisability of assessing detergency

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[2] *Chemist.*

on the basis of such tests alone. Moreover, they measure an over-all effect which may or may not be indicative of performance in use and do not clearly distinguish between soil removing and suspending power as defined above. For example, if a given detergent solution gives good over-all removal of soil from the fabric it may be concluded that the detergent solution has good soil removing and good suspending power; on the other hand, if the soil is not effectively removed it is not known whether the failure is due to poor soil removing power or to poor suspending power.

The suspending power of a detergent solution is thus of considerable importance in determining the over-all detersive efficiency, and in certain cases may have an even greater influence on the final result than the actual soil removing power. It has been shown (3, 20) that redeposited soil is frequently more difficult to remove than the original soil, and also that the best detergent for removing soil is not necessarily the most efficient in preventing its redeposition.

Literature references to the measurement of suspending power of detergent solutions are limited in number. McBain and coworkers (15) proposed a method involving measurement of the amount of carbon passing through a filter paper used to filter a suspension of carbon in the detergent solution.

Fall (10) attempted to measure suspending power by suspending manganese dioxide in the detergent solution and determining by chemical analysis the amount of suspended material.

Snell (24) carried out work similar to that of Fall using a complex soil containing powdered burnt umber impregnated with a mixture of cottonseed oil, mineral oil, and oleic acid.

Carter (3) and Vaughn and Vittone (30) carried out measurements similar to those used in the present study, but their work is concerned chiefly with the suspending powers of "soap builders" (viz., alkalies used to increase the effectiveness of soap).

Powney and Noad (18) have investigated the suspending powers with respect to the mineral ilmenite ($FeO.TiO_2$) of various soaps, builders, and a few soap-builder mixtures ("built soaps").

Vaughn and Smith (29) carried out measurements of "whiteness retention" on a series of detergent formulations containing a synthetic detergent of the alkyl–aryl type, alkaline builder, and sodium carboxymethyl cellulose by a method similar to that used in the present work, employing as their soiling agent "Aquablak B", a commercial dispersion of carbon black in water containing an unspecified dispersing agent.

The present paper gives data relating to the suspending power with respect to a number of commercially available carbon blacks and other soiling materials of a series of sodium soaps of fatty acids most commonly occurring in commercial soaps.

Experimental

Materials Used

Soiling Materials

Since the rubber industry is the largest user of carbon blacks, these have been classified according to their use in rubber compounding. There are three fundamental properties of carbons (viz., pH, surface area, and "structure") which appear to determine their behavior in such compounds (7, 8, 27, 33), and these properties have been employed in the present paper for the purpose of characterizing the carbons used. These are listed in Table I, the data given being obtained from manufacturer's publications (8, 27, 34).

TABLE I

Properties of colloidal carbons

Carbon	pH	Average diameter, $m\mu$	Area sq. meter/gm.*	Structure Index
Royal Spectra	2.8	9	285	100
Standard Micronex (uncompressed)	4.5	28	95	100
Statex B	10.0	36	75	100
Acetylene Black	8.0	40	65	300
P-33	8.0	90	37	60
Lampblack	4.0	97	23	200

**Recalculated from manufacturer's data which are given in acres per pound.*

With the exception of acetylene black which is produced by Shawinigan Chemicals Ltd., Shawinigan Falls, P.Q., and P-33 produced by the Thermatomic Carbon Co., Sterlington, La., the carbons listed are manufactured by the Columbian Carbon Co., 41 East 42nd St., New York.

A seventh preparation of carbon (viz., "Aquadag") and a titanium pigment "Air-floated Ilmenite Black" were also investigated. Aquadag, manufactured by Acheson Colloid Corp., Port Huron, Mich., contains graphite particles having a maximum diameter of 4μ, and a mean diameter of 1μ or less. It is supplied as an aqueous paste in which the graphite particles are suspended with the aid of ammonia and dextrinous materials (1). Ilmenite Black, supplied by British Titan Products Co. Ltd., Billingham, England, was used by Powney and Noad (18) in suspending power measurements and is claimed by these authors to be of remarkable uniformity, the majority of the particles having diameters of approximately 1μ. The ilmenite used in the present study was given a preliminary extraction with hydrochloric acid, followed by a thorough washing with water, in accordance with the recommendations of Powney and Noad.

Soaps

Sodium soaps of lauric, myristic, palmitic, stearic, and oleic acids were prepared from Kahlbaum or Schuchardt fatty acids, following the method described by Powney (17). The melting point, acid number and "percent purity" calculated from the acid number of the fatty acids are listed in Table II. The alcohol used in the preparation of the soaps was freed from aldehydes by refluxing for 30 min. with powdered zinc and sodium hydroxide, followed by distillation.

TABLE II

CHARACTERISTICS OF FATTY ACIDS USED IN PREPARATION OF SOAPS

Acid	Melting point, °C.	Acid number mgm. KOH/gm. acid	Purity, %
Lauric	44.0	281.5	100.5*
Myristic	53.0	244.0	99.3
Palmitic	62.5	216.5	98.8
Stearic	69.0	196.5	99.4
Oleic	—	193.5	97.4

**Indicates presence of traces of lower molecular weight acids.*

Fabric Samples

Fully bleached cotton fabric (nainsook, having a thread count of 100 × 100 and a weight of 2.7 oz. per sq. yd.) was desized by immersion for half an hour in boiling 1% acetic acid, followed by three rinses in cold distilled water. The fabric was then immersed for half an hour in boiling distilled water and rinsed four more times in cold distilled water. This treatment resulted in a negligible amount of chemical damage as measured by its effect on the cuprammonium fluidity of the material. After drying, the fabric was cut into pieces 3 in. by 4 in. with the longer dimension in the warp direction.

METHOD

The procedure consisted essentially of measuring photometrically the decrease in whiteness of the cotton samples after shaking in a suspension composed of carbon particles and the aqueous detergent solution. For this purpose 0.250 gm. of the dry carbon* was weighed out and transferred to a 415 ml. vacuum bottle which had been previously warmed to 2 to 3 degrees above the working temperature. Exactly 250 ml. of soap solution of the required concentration and temperature was added and the bottle was closed with a stopper covered with tin foil. The bottle was shaken for 20 min. in a mechanical shaker, having a reciprocating motion with a stroke of 3 in. and

**Aquadag is supplied as an aqueous paste containing 22.3% solids by analysis. In this case the paste was diluted so that 150 ml. contained 0.25 gm. of solid, and the concentration of the added soap solution was adjusted so that the total volume of soap solution plus suspension was 250 ml.*

a speed of 105 cycles per minute. The fabric sample, previously wetted out in boiling distilled water, was then added and the bottle shaken for a further 20 min. At the end of this period the sample was removed, rinsed lightly in distilled water at the working temperature, and dried in a horizontal position on an aluminum screen. A second fabric sample was then shaken in a similar manner in the same suspension.

After drying, the fabric samples were ironed between damp cloths and their reflectance was measured with a Hunter reflectometer (12), using a single thickness of fabric backed by a piece of white cardboard. One reading was made on each side of the sample and each experimental value for suspending power was obtained by averaging at least eight readings. The following formula was used in calculating suspending power:

$$S.P. = \frac{B - B_w}{B_0 - B_w} \times 100,$$

where B = average reflectance of fabric at the end of experiment,
B_w = "water value" (i.e., average reflectance of the fabric when shaken in a suspension of the carbon in distilled water),
B_0 = original reflectance of fabric.

On this basis a suspending power of 100% represents no deposition of carbon on the fabric, and 0% represents the suspending power of distilled water. Negative values represent a suspending power less than that of distilled water.

Preliminary Experiments

No measurable difference was obtained in the reflectance of two fabric samples shaken consecutively in the same suspension, the amount of carbon removed by the first sample being negligibly small in comparison with the total amount present.

In the course of determining the most satisfactory method of carrying out the photometer readings, it was found that there is a difference of approximately 2 units between readings on the same sample after rotation through 90°, while readings taken after 180° rotation showed no appreciable difference. Hence the reflectance of the samples was always determined with the longer dimension in a horizontal position.

In order to check the reproducibility of the method, a series of six bottles of suspension (24 readings) were run under identical conditions. It was found that the maximum deviation from the mean did not exceed ± 3%, and the average deviation was somewhat less than ± 2%.

The degree of temperature control afforded by the vacuum bottles over a total shaking time of 60 min., with the bottles being opened at 20-min. intervals, was such that the drop in temperature of the solution was approximately 1° at 40° C. and 2° at 65° C.

Measurement of Suspending Power with Various Suspended Materials

Suspending power measurements were carried out at 60° C., using sodium laurate and sodium stearate at varying concentrations and each of the soiling materials selected for investigation. The results are shown graphically in Fig. 1.

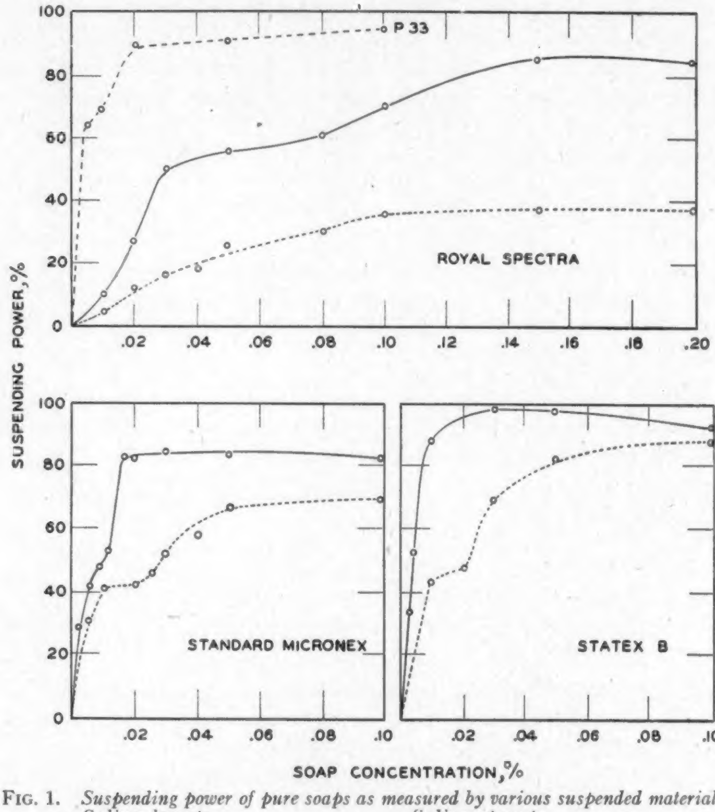

FIG. 1. *Suspending power of pure soaps as measured by various suspended materials. Sodium laurate - - - - - - - - - - - - - -. Sodium stearate ————————.*

For those carbons which have a normal or subnormal structure (structure index 100 or less, see Table I) the suspending power of either soap at any given concentration increases with increasing size of the carbon particle (i.e., there seems to be less tendency for the larger particles to cling to the fabric). The high structure carbons, acetylene black and lampblack, show anomalous behavior. The particle diameter of acetylene black is similar to that of Statex B, but the suspending power at any soap concentration as measured by acetylene black is considerably lower than the suspending power of the same solution as measured with Statex B. Similarly lampblack is

comparable in size to P–33, but again the suspending power is lower. It may be concluded that the chain or network structure of these carbons enables them to cling more tenaciously to the fabric. It may be noted that, in addition to differences in degree of indicated suspending power, the different soiling materials show considerable variation in the form of curve produced with the same soap solution.

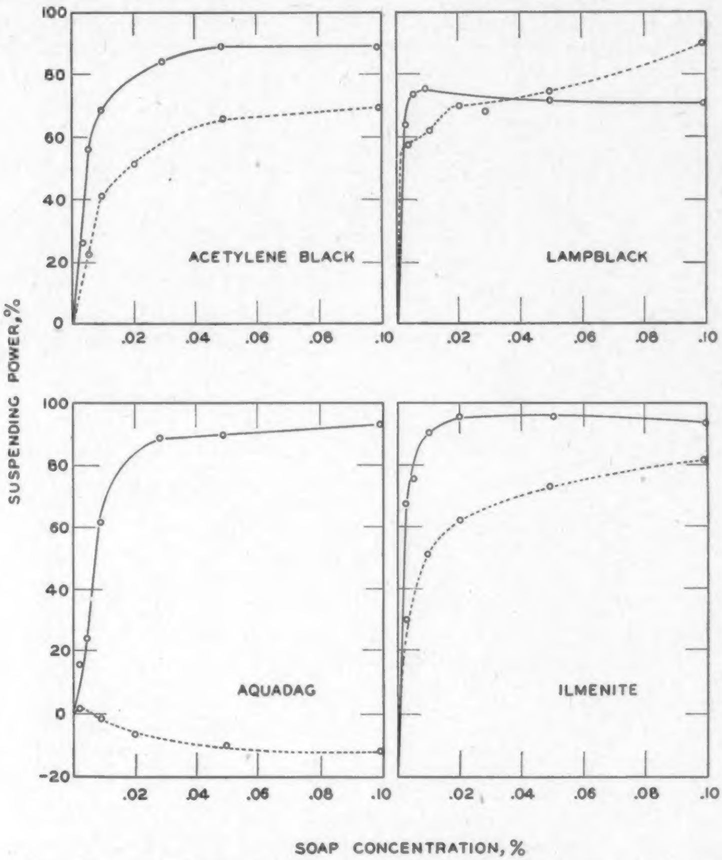

FIG. 1 (*continued*). *Suspending power of pure soaps as measured by various suspended materials. Sodium laurate* - - - - - - - - - - -. *Sodium stearate* ————.

While it was desirable as a preliminary step to study the suspending power of soaps towards various types of carbon, it was necessary to select a single type of carbon for further investigation in order to keep the magnitude of the work within reasonable limits. Consequently Standard Micronex was used in all subsequent work on the measurement of suspending power. This material was satisfactory with respect to reproducibility of results, gave a

fair degree of differentiation between various soaps, and a degree of soiling of the fabric such that a wide range of suspending powers could be measured.

Effect of Chain Length on the Suspending Power of Soaps

The suspending power of the saturated sodium soaps having chain lengths of 12 to 18 carbon atoms and of sodium oleate (C_{18}) was determined at 60° C. over a soap concentration range of 0 to 0.1%. The results are given in Fig. 2.

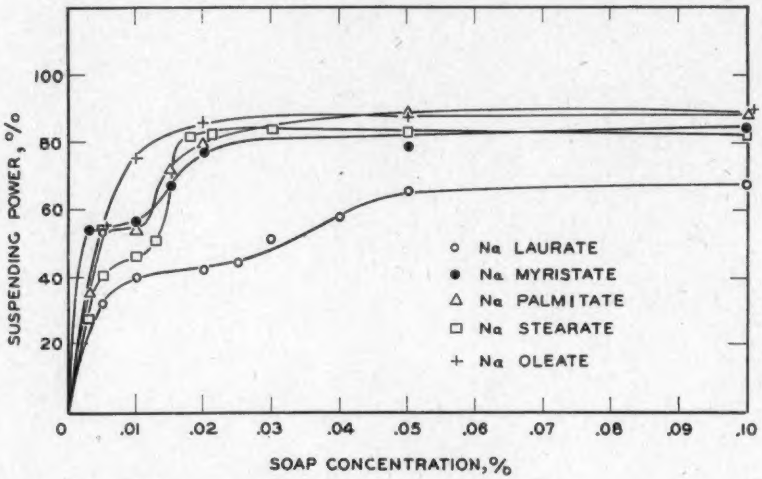

FIG. 2. *Suspending power of pure soaps at 60°C.*

Considering the saturated soaps, it may be seen that there are only minor differences between myristate, palmitate, and stearate, all of which show higher suspending power than the laurate.

The curves for the saturated soaps all show a peculiar inflection at low concentrations, but there seems to be no evidence of it with sodium oleate. Data for the critical micelle concentration of the saturated soaps, obtained from various sources in the literature (9, 13, 14, 26), are summarized in Table III. Some of the data are for potassium soaps, but values for the corresponding sodium soaps, expressed on a molar basis, are said to be identical (13). In spite of the variation in data obtained by different methods, it would appear that the concentration range employed in the present work (0–0.1%) does not include the critical micelle concentration for laurate and myristate, but does include it for palmitate and stearate. Yet curves of similar form were obtained with all these soaps, which would seem to indicate that the inflection is not related to micelle formation. However, it has been shown (19, 31) that carbon not only adsorbs considerable amounts of soap from solution, but also preferentially adsorbs fatty acid or acid soap so that the residual solution contains an excess of alkali. The effect of such adsorp-

tion on the critical micelle concentration of the residual solution is difficult, if not impossible, to predict.

The suspending power of sodium oleate appears to be somewhat better than that of sodium stearate at all concentrations. This is not in agreement with Powney and Noad (18) who found that the double bond in sodium oleate was equivalent, in its effect on suspending power with respect to the mineral ilmenite, to a shortening of the effective chain length. This was

TABLE III

CRITICAL MICELLE CONCENTRATION OF THE SATURATED SOAPS AT 50–70°C.

Soap	Critical micelle concentration	
	Molar	% (as sodium soap)
Laurate	0.020–0.042	0.44–0.93
Myristate	0.007–0.010	0.18–0.25
Palmitate	<0.001–0.0032	<0.028–0.089
Stearate	0.0008	0.024

confirmed by the present authors in a limited series of experiments with ilmenite, and serves to emphasize further the influence of the particular type of soiling material on the suspending power data obtained.

Szegö (28) in measurements of detergent power found that detergency increased with increasing chain length of the saturated soaps up to C_{16}, but the detergent power of the C_{18} soap was considerably lower. He attributes this to the low solubility of the stearate. He also found that the detergent power of sodium oleate is slightly higher than that of sodium palmitate (C_{16}) and considerably higher than that of the stearate. While measurements of detergency are not strictly comparable with the present measurements, the similarity in results is of interest.

Influence of Temperature on Suspending Power

Suspending power data were obtained for sodium laurate and sodium oleate solutions over the concentration range 0–0.1% and at temperatures of 25°, 40°, 60°, and 80°C. These results are shown in Figs. 3 and 4. In addition, data were obtained for 0.1% solutions of sodium myristate at 50°, 60°, and 80°C. and for sodium palmitate and sodium stearate at 60° and 80°C. Measurements at the lower temperature were not attempted with these soaps owing to their limited solubility. The results are given in Table IV.

It is interesting to note that sodium laurate and sodium myristate have a negative temperature coefficient of suspending power (i.e., the suspending power decreases with increasing temperature), sodium palmitate and sodium stearate have a positive coefficient, and sodium oleate has a zero or very small coeffi-

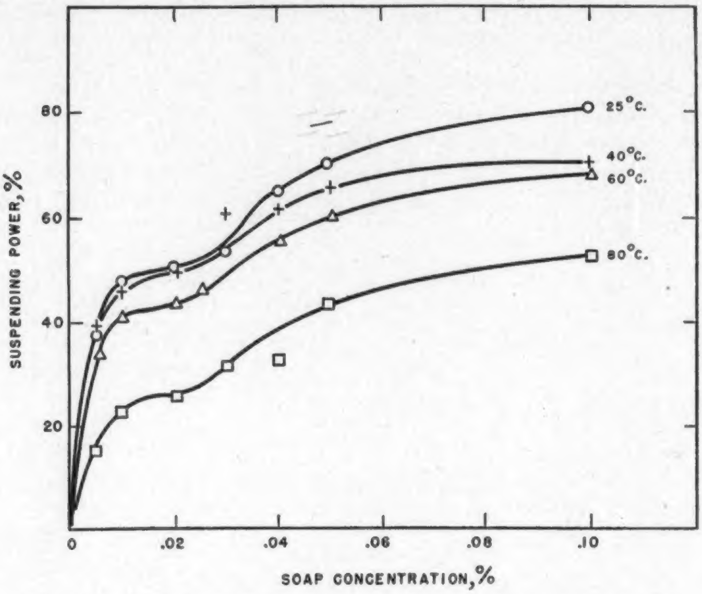

FIG. 3. *Influence of temperature on the suspending power of sodium laurate.*

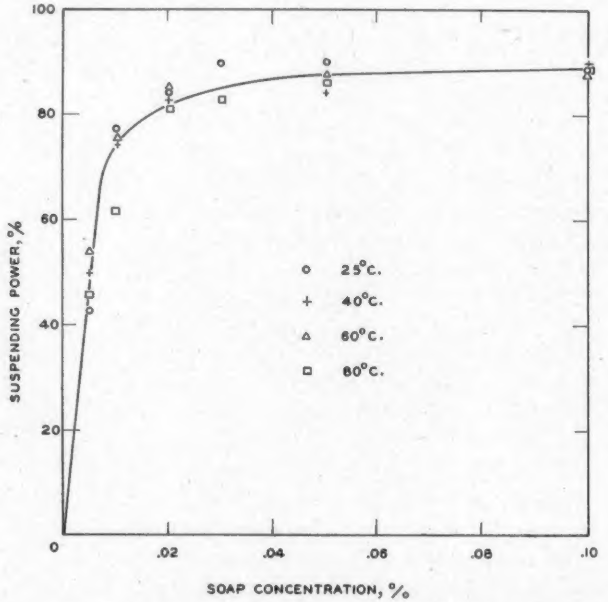

FIG. 4. *Influence of temperature on the suspending power of sodium oleate.*

TABLE IV

EFFECT OF TEMPERATURE ON THE SUSPENDING POWER OF 0.1% SOAP SOLUTIONS

Soap	Suspending power, %			
	25°C.	40°C.	60°C.	80°C.
Sodium laurate	80.0	69.7	67.5	52.2
Sodium myristate	—	85.4	84.0	77.6
Sodium palmitate	—	—	88.2	94.5
Sodium stearate	—	—	82.0	95.6
Sodium oleate	88.7	89.9	87.9	88.5

cient over the temperature range investigated. This latter fact is confirmed by Powney and Noad (18) who concluded that the suspending power of sodium oleate was independent of temperature changes over the range 19–74°C.

Somewhat analogous temperature effects with respect to the wetting power of various sulphosuccinic acid esters have been reported by Caryl (5), who found that the more soluble esters lost wetting power on heating while the less soluble ones improved in wetting power. He attributed these effects to a disturbance of the balance between polar and nonpolar portions of the molecule caused by variations in temperature.

From the data of Table IV it may be seen that the suspending power of sodium laurate at 25°C. compares favorably with that of sodium stearate at 60°C., while at 80°C. the stearate is much superior to the laurate. Similarly, the suspending powers of sodium myristate and sodium stearate are about equal at 60°C., but at 80°C. the stearate is superior. It is thus apparent that the chain length of the saturated soaps at which maximum suspending power is obtained depends largely on the working temperature. It is probable that for each soap there is an optimum temperature, or range of temperatures, at which maximum suspending power is attained, and that deviations from the optimum temperature in either direction result in decreased suspending power.

The effect of temperature on the suspending power of sodium oleate is obviously very small, and the precision of the method employed is not sufficient to measure it with any degree of accuracy. However, it may be significant that both our data and those of Powney and Noad (18) could be interpreted as showing a slight concavity toward the concentration axis, indicating that there is an optimum temperature for this soap too, but that the suspending power maximum extends over a broad temperature range.

Colt and Snell (6) have pointed out that in any detergent process there are four "dispositions" of the detergent compound, viz: (1) neutralization of the hardness of the water, (2) adsorption by carbon or other constituents of the

soil, (3) adsorption by the fabric, and (4) a minimum residual concentration necessary for satisfactory detergency.

In the present case Factor (1) does not apply since distilled water was used throughout.

The adsorption of soap by carbon has been studied in some detail (19, 31). It was found that the presence of 1 gm. of carbon (Standard Micronex) in 250 ml. of 0.1% soap solution reduced the concentration of sodium laurate solutions by about 10%, and of sodium stearate solutions by about 45% of their initial values. At lower initial concentrations a still greater proportion of the soap was adsorbed, the values at 0.02% initial concentration being 30 and 90% for sodium laurate and sodium stearate respectively. While the ratio of soil (carbon) to soap solution employed in these measurements was higher than that used in the present work, and considerably higher than would normally be encountered in practical detergent operations, it is nevertheless apparent that appreciable amounts of soap may be removed from solution as a result of adsorption by the soil particles. It was also shown that carbon preferentially adsorbs fatty acid or acid soap from neutral soap solutions, so that the residual solution may contain a considerable excess of free alkali.

The adsorption of soap by soil particles may be considered advantageous from the standpoint of improved suspending power, and hence of over-all detergency, since the adsorbed soap ions impart negative charges to the particles, and thus, owing to electrostatic repulsion, tend to prevent their coalescence and deposition.

The adsorption of soap by various textile fibres has also been studied (32), and it was found that, with respect to cotton fabric, the reduction in concentration of a 0.1% soap solution at a load/solution ratio of 1/25 varied from about 2% to 7% for various soaps. In the present case, where the load ratio was of the order of 1/180, the reduction in soap concentration due to adsorption by the fabric is obviously negligible, but under conditions of practical detergency, where much higher load ratios are employed, it may become appreciable. The adsorption of soap by the fabric is of considerable importance in relation to suspending power, since the adsorbed soap ions impart negative charges to the fibers, and thus enable them to repel the negatively charged soil particles.

Many workers in the field of detergency have postulated the existence of surface forces which cause soil particles to adhere to fabric surfaces and to each other. While little is known of the nature of these forces, it is probable that their magnitude is determined largely by the adsorption of soap ions at the fabric–solution and soil–solution interfaces (2). The degree of soiling of the fabric depends upon two factors: (*a*) the number of carbon particles which collide with the cotton, and (*b*) the proportion of particles which adhere to the fabric after the collision. The number of collisions is influenced by the magnitude of the repulsive electrostatic forces between the carbon particles and the

fabric surface, both of which are negatively charged as a result of the adsorption of soap. A carbon particle must approach within a certain minimum distance of the fabric surface before the surface forces referred to above become operative. The magnitude of these forces thus determines the minimum distance to which a particle may approach the fabric without actually adhering to it.

It may thus be concluded that the suspending power of a soap solution is dependent very largely on the adsorption of soap ions at the various interfaces concerned. The minimum residual concentration necessary for satisfactory detergency (Factor 4 above) would appear to be merely the minimum concentration necessary to maintain the adsorption equilibria at the required levels.

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